## *The spatially-differentiated total nitrogen budget for Great Britain*

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# The spatially-differentiated total nitrogen budget for Great Britain

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*Dedicated to*

My grandpa who sacrificed so much for our family during his lifetime and always encouraged me to pursue further studies. I can never forget you shouting *Luolixie* and reminding me that education can change your destiny.

## Abstract

To understand Nitrogen (N) cycling, mechanisms of N transformation, and factors that influence N pathway, N budgets at different scale were constructed in this thesis. This thesis addresses N cycling in Great Britain (GB) through four discrete investigations at the national to catchment scale. At the national scale, a spatially-differentiated N budget for GB was constructed at a 1 $km^2$ grid scale, which showed that both sink and source areas exist in GB. The spatial N budget across GB ranged from -21 ($\pm$3) to 34 ($\pm$5) tonnes N/$km^2$/yr, with 66% of grid squares identified as source areas and 34% identified as sink areas. A spatial N budget of the Trent catchment was constructed by using local rather than country level N flux data, revealing range of -16 ($\pm$5) to 32 ($\pm$6) tonnes N/$km^2$/yr. To test where N accumulation occurred, 24 locations were selected for soil sampling to test the C/N for different soil depths. The study demonstrates that depth profile has a significant affect upon C/N ratio between sink and source under grassland, however, this measure tested for N accumulation did prove to be significant under grassland but not under arable.

Between 1990 and 2015 the temporal changes in the N budget of the Trent catchment varied from -4.3 ($\pm$0.7)$\times 10^4$ to 3.5 ($\pm$0.5)$\times 10^4$ tonnes N. N accumulation in the Trent catchment is likely continue at a similar magnitude in the future until the soil of Trent catchment reaches saturated state. The research also updates the nitrate flux model at country scale and finds that catchment area, organic soil, each land use area and gas emission, all have a positive relationship with nitrate flux whereas N deposition and rainfall, both have a negative relationship with nitrate flux.

# Declaration

I confirm that no part of the material presented in this thesis has been submitted by me or other person for a degree in this or other university. In all cases, where it is relevant, material from the work of others has been acknowledge.

## Publications

1. Fan, Xiangwen, Fred Worrall, Lisa M. Baldini, and Tim P. Burt. A spatial total nitrogen budget for Great Britain. Science of The Total Environment (2020): 138864.

2. Fan, Xiangwen, Fred Worrall, Lisa M. Baldini, and Tim P. Burt. (submitted) Spatial variability in the Trent catchment nitrogen budget: Identify areas of nitrogen accumulation and loss. Geoderma.

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# Glossary of terms

**Acronyms**:

BNF:biological nitrogen fixation

CEH:centre for ecology & hydrology

CoFID:composition of foods integrated dataset

DOC:dissolved organic carbon

DON:dissolved organic nitrogen

DIC:dissolved inorganic nitrogen

Defra:department for environment food & rural affairs

HMS:harmonised monitoring scheme

NAEI:national atmospheric emission inventory

OSPAR:Oslo and Paris Commission

PON:particulate organic nitrogen

TON:total organic nitrogen

POC:particulate organic carbon

**Symbols**:

N:nitrogen

$NO_3^-$:nitrate

$NO_2^-$:nitrite

$NH_3$:ammonia

$NH_4^+$:ammonium

$N_2$:di-nitrogen(gas)

$N_2O$:nitrous oxide

NO:nitric oxide

Nr:reactive nitrogen species

$NO_2$:nitrogen dioxide

C:carbon

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# Chapter 1

# Introduction

## 1.1 Introduction

Nitrogen (N) is a naturally occurring element that is essential for growth and reproduction in both plants and animals. It is found in amino acids that make up proteins, in nucleic acids, that comprise the hereditary material and life's blueprint for all cells, and in many other organic and inorganic compounds. N comprises about 78 % of Earth's atmosphere, which is the largest source of N. In the environment, N takes a wide variety of chemical forms including organic N, inorganic N and inorganic N gas. N valence states ranging from -3 (in $NH_3$) to +5 (in $NO_3^-$) and, as a result, N can be converted into a range of different forms as it circulates through the atmosphere and terrestrial and marine ecosystems. Therefore, the N cycle describes the linkage between the atmosphere, the land, and the oceans. Anthropogenic N inputs have changed how N cycles between the atmosphere, the land and the ocean.After World War II the natural rate of N fixation, production of fertiliser, cultivation of leguminous crops, and industrial N have increased to meet the world's growing hu-

man population. Industrial era human activities have disrupted the potential for the steady-state condition in the N cycle on land (Galloway et al. 2004; Liu et al. 2010). Once too much N is lost to the environment, the N moves through the atmosphere, forest, grassland and water negatively impacting both people and ecosystems (e.g., blue baby (Townsend et al. 2003), carbon (C) storage in the biosphere (Townsend et al. 1996), terrestrial plant diversity (Bobbink et al. 2010; Stevens et al. 2010) and global climate change (Vitousek 1994)).

Disturbance of the N cycle by human activity has become the third major threat to our plant after biodiversity loss and climate change (Giles 2005). Excessive N is known to have a variety of detrimental effects on the environment including an increasing incidence of 'red tides' (too much N causing rapid algal growth) (Van Drecht et al. 2003), acid rain (N reacts with water,oxygen and other chemicals to form nitric rain) (Driscoll et al. 2001), biodiversity reduction (N deposition increases the availability of a major limiting nutrient, accelerating the leaching loss of base cations and favouring certain plant species over others) (Cardinale 2011) and greenhouse induced global warming (increasing emissions of nitrous oxide, a powerful greenhouse gas) (Vitousek et al. 1997). Investigating N input, migration, transformation and output can help people to better understand what factors influence N pathways and mechanisms of transformation and migration of N. This knowledge can inform N management strategies and government policies aimed at reducing N pollution. This chapter describes the study background and previous literature and provides a general summary of the aim, methodology, and content of this Ph.D. dissertation.

## 1.2 Background

There is a long history of N limitation in the terrestrial ecosystem before human development of reactive N in the form of synthetic fertilisers. The global rate of reactive nitrogen (Nr) production for fertilisers has increased sharply since 1960 (Robertson and Vitousek 2009). Wherever N enters the ecosystem in excessive amounts, there are environmental concerns. As a result, the biogeochemical pathway of N at the Earth's surface and the environmental impacts have become an important focus of regional global change research. Scientific Committee on Problems of the Environment (SCOPE), Intergovernmental Panel on Climate Change (IPCC), International Geosphere-Biosphere Program (IGBP) and Organisation for Economic Co-operation and Development (OECD) started to focus on the research of N cycles. At present, several studies in the UK (Worrall et al. 2016b), America (Van Breemen et al. 2002, Brazil (Boyer et al. 2002), Korea (Parfitt et al. 2006), New Zealand (Filoso et al. 2006), Japan (Yoshikawa and Shiozawa 2008) and China (Ti et al. 2012) have investigated N cycle dynamics to understand every pathway in the N cycle, its quantity, environmental effects, and controls.

From 1945, agriculture in developed countries faced high pressure to produce higher yields from crops. To increase agricultural production, N inorganic fertiliser was developed through the Haber process in 1909 and eventually used in great quantities to help productivity (O'Riordan and Bentham 1993). In the UK, the use of fertiliser rose by 900% from the mid-1940s to the mid-1980s (refer). During this period, crop cultivation and N emission from fossil fuel combustion also increased

sharply. Excessive anthropogenic Nr input may lead to large fluvial N loss to surface water and groundwater raising concerns about health risks (N dioxide inflames the lining of the lungs, and it can reduce immunity to lung infections) and water pollution (overstimulation of growth of aquatic plants and algae) (Burt et al. 1993). As a result, several studies across the UK were undertaken to assess the extent of Nr pollution including: i) eutrophication of lakes, rivers and reservoirs in British (Collingwood 1977); ii) soil acidification caused by N leaching the nitrate leach away from the root zone leaving behind hydrogen ions thereby increasing soil acidity and deposition in various parts of the UK (Goulding 2016); iii) nitrate concentrations of surface water above the EU drinking water standards observed in Leet water of Scotland with implications for public health (IOH 1996). These examples of N pollution are detrimental to the natural environment, human health and society. For example, when algal blooms flourish, they cut out light to the subsurface; the decomposition of the algae depletes oxygen in the water, and some of algae are toxic to fish and mammals (Addiscott 1996). Soil acidification caused by excessive N input has resulted in forest decline in Europe (Matzner and Murach 1995). High nitrate concentrations in drinking water can cause two health problems in humans: 'blue-baby' syndrome methemoglobinaemia caused by nitrites binds to the hemoglobin in the body and gastric cancer (Knobeloch et al. 2000). Therefore, it is important to determine the movement of N through input and output pathways, the factors controlling N pathways, and assess trends in the N budget to provide accurate N management to control N loss.

## 1.3 Biogeochemistry

### 1.3.1 Reactive nitrogen

Nr includes all forms of N that are biologically, photochemically, and radiatively active N compounds in the Earth's atmosphere and biosphere. Compounds of N that are reactive include inorganic reduced forms of N (ammonia [$NH_3$] and ammonium [$NH_4^+$]), inorganic oxidized forms (nitrogen oxide [NOx], nitric acid [$HNO_3$], nitrous oxide [$N_2O$], nitrite[$NO_2^-$] and nitrate [$NO_3^-$]) and organic compounds (urea, amines, proteins, and nucleic acids) (Galloway et al. 2003). Unreactive nitrogen ($N_2$) makes up 78% of the atmosphere which is very common and plentiful, but only by converting $N_2$ to one of the above compounds can it become available to the biosphere. Nr can be created both naturally and synthetically (Galloway et al. 2003). Nr can be generated naturally by two processes: lightning and biological nitrogen fixation (Galloway et al. 2003). The triply bonded nitrogen molecule is inert. To break it apart so that its atoms can combine with other atoms requires the input of substantial amounts of energy. Three processes are responsible for most nitrogen fixation in the biosphere. High energy lightning strikes break apart the triply bonded nitrogen molecule enabling the constituent atoms to combine with oxygen in the air forming nitrogen oxide molecules. These molecules dissolve in water, forming nitrates, and are carried to the Earth's surface in rainfall. Global biological nitrogen fixation (BNF) produced 0.9-1.3 $\times 10^8$ tonnes N/yr in the absence of human activity Galloway 1998. A further 1.5 $\times 10^8$ tonnes N is fixed by human activities through the combustion of fossil fuels (N contained in fossil fuel emit), N fertiliser

application and artificial widespread of legume crops (Galloway 1998). Biological N fixation and denitrification were approximately equal in the Pre-industrial era (before 1750), therefore, Nr did not accumulate in environmental reservoirs (Ayres et al. 1994). However, doubling of the annual rate of anthropogenic N fixation over the past 150 years has led to an accumulation of Nr in the environment at both local and regional scales (Galloway 2005). The most dramatic increase in anthropogenic Nr production has occurred since World War II with the advent of synthetic fertilisers in 1909 needed to feed the World's growing population (Galloway 2005) (Figure 1.1).

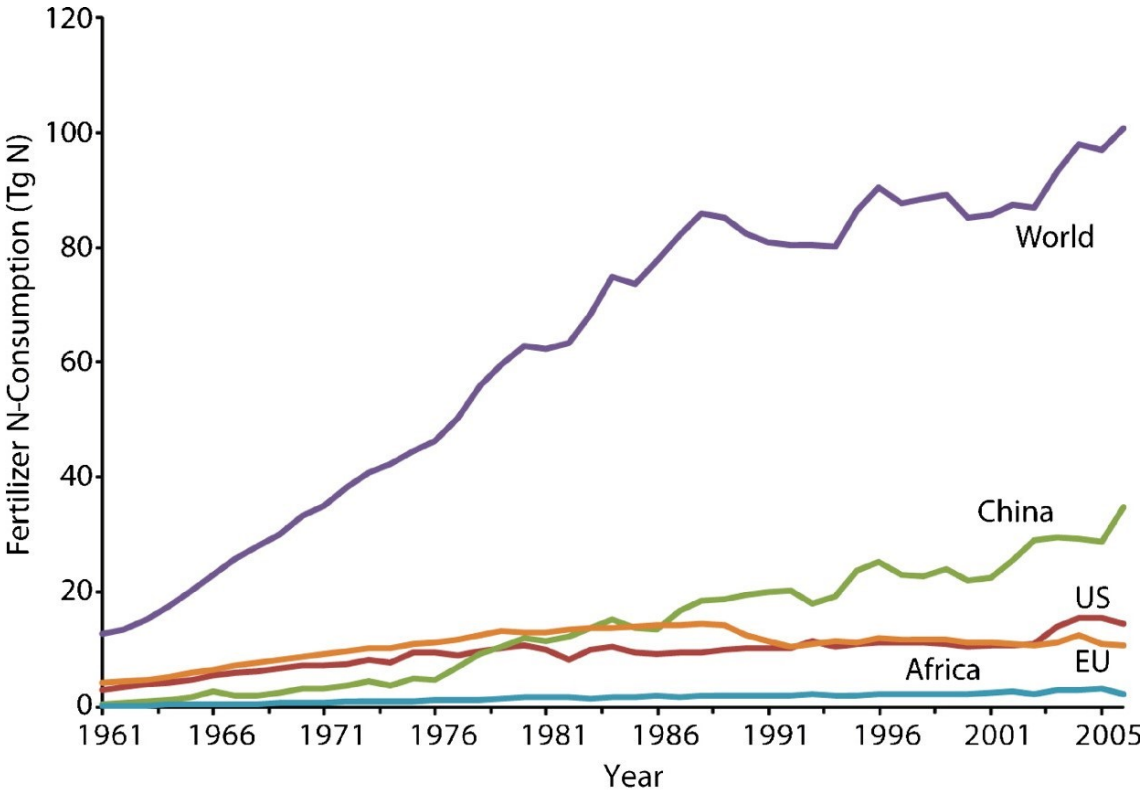


**Figure 1.1:** Production of nitrogen fertiliser globally and country. *Source: From Robertson et al. (2009).*

Global anthropogenic Nr input increased from 0 tonnes N/yr in 1860 to an

estimated 1.65 $\times 10^8$ tonnes N/yr in 2050 (Galloway 2005). In the UK, anthropogenic Nr input has decreased from 2.3 $\times 10^6$ tonnes N/yr in 1990 to an estimated 2.0 $\times 10^6$ tonnes N/yr in 2020 (Worrall et al. 2016a). N fertiliser input represents the largest contribution of total N input, therefore, a decrease in N fertiliser use from 1.5 $\times 10^6$ tonnes N in 1990 to 0.8 $\times 10^6$ tonnes N in 2020 is largely responsible for the predicted trend (Figure 1.2). Combustion of fossil fuels, another anthropogenic Nr source, rose from 2 $\times 10^5$ tonnes N/yr in 1990 to an estimated 3 $\times 10^5$ tonnes N/yr in 2020. Although total anthropogenic Nr has decreased in recent years in the UK, anthropogenic Nr still accounts for the largest proportion of all N inputs (Worrall et al. 2016a).

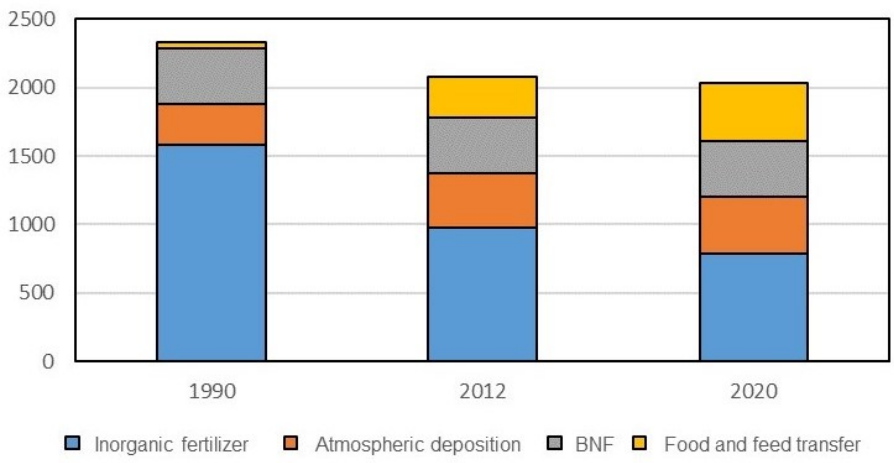


**Figure 1.2:** The predicted reactive nitrogen input change over 1990 -2020 in UK.

### 1.3.2 The global cycles of nitrogen

The most abundant form of N at the surface of the earth is $N_2$, which is not biologically available to most organisms. Biochemical transformations of N (e.g. through microbial activity) can convert (or 'fix') atmospheric $N_2$ to biologically available N

compounds (Rosswall 1982). Figure 1.3 presents the global N cycle that connects the atmosphere, land, and oceans. The variety of chemical forms including organic N, $NH_4^+$, $NO_2^-$, $NO_3^-$, $N_2O$, NO and $N_2$. According to Galloway et al. (2003), the process in the N cycle was transformed N from one form to another. $N_2$ is converted into N organic compounds by N fixing bacteria (e.g. free-living in water, soils and sediments or symbiotic association with the roots of plants) and stored in the N-fixing plants. The $NO_3^-$ in the atmosphere can be transferred to surface land via dry

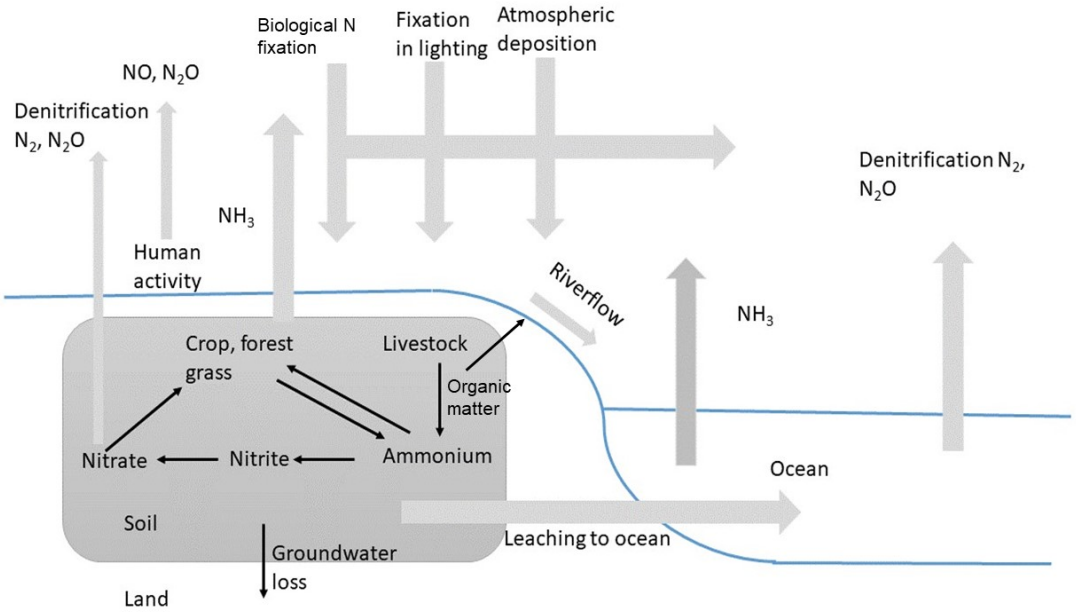


**Figure 1.3:** The global nitrogen cycle.

deposition or wet deposition. Haber-Bosh and fossil fuel combustion can transfer convert $N_2$ to Nr and the process detail discussed in the last section. N fertiliser (including produced by the Haber-Bosch process and animal manure) is applied to global agroecosystem crops which transfer to human and livestock via food and feed (Smil 1999; Smil 2004). Part of the N fertiliser application is lost to the atmosphere as $NH_3$, NO, $N_2O$, $N_2$ or stored in the soil (Erisman et al. 2007). The N moves

between animals, soil and crop in an internal N cycling - the harvested plant is fed to livestock and livestock manure is applied to the soil which is then assimilated by the crop. Plants also assimilate N derived from internal cycling and decomposition of dead materials in the soil. The N applied to the biosphere is lost through denitrification ($N_2$ and $N_2O$) and other gaseous pathways (NOx) in terrestrial soils and the ocean. N stored in the soil can be lost to surface water, groundwater or continues to be stored in the soil. Galloway et al. (2004) used the term 'nitrogen cascade' to describe the sequence of N forms as it moves along different biogeochemical pathways. Not all N cascades at the same rate. Nr accumulates in some reservoirs increasing its effects on the environment.

## 1.4 N budget ——input and output pathway

Surface water nitrate pollution has drawn considerable attention in the literature (e.g. Jaworski et al. 1992; Howarth et al. 1996; David et al. 1997; Howden et al. 2011b). Previous studies, however, have largely focused on the impacts of N input on estimated N fluvial flux with only arable and grass output pathways considered as grass land and arable land have a close relationship with N fluvial loss. In response to the dearth of research addressing other N pathways, Boyer et al. (2002) considered all significant N output pathways (N fluvial flux, denitrification, $NH_4$ volatile, food and feed transfer) and soil N storage to estimate the link between fluvial N flux and different N component. In the UK, Worrall et al. (2016a) and Muhammed et al. (2018) estimated the N budget of the UK which, in addition to the pathways considered by Boyer et al. (2002), also considered the role of animal manure and dead

crop plant recycling. Other research has focused on the increase in N loss caused by anthropogenic N input and the associated environmental effects (Yoshikawa and Shiozawa 2008; Lewis Jr et al. 2011). As a result of these previous studies, N inputs considered for this thesis include biological N fixation (BNF), atmospheric deposition, inorganic fertiliser, and food and feed N transfers. N outputs considered include atmospheric emissions, denitrification, N fluvial flux at soil source, direct sewage N flux, N loss to groundwater (groundwater loss), industrial N emissions, crop removal, and gas emissions from sewage treatment plants.

### 1.4.1 Biological Nitrogen Fixation

The BNF is a major N input pathway which occurs in natural and agricultural ecosystems. BNF rates are calculated according to crop type (including grass and forest) and combined to derive the overall BNF rate. BNF flux is not uniformly distributed between ecosystems with N fixation in agricultural ecosystems accounting for nearly half of the total N fixation in land (Herridge et al. 2008). Natural N fixation (by free living and symbiotic bacteria) is limited by a range of biotic and abiotic factors. The biotic N fixation dwarfs abiotic fixation by lightning as the source of fixed N. The current available N from BNF is inadequate to supply all of the requirements of growing crops making it necessary to assimilate N from fertilisers or atmospheric N deposition in soils. Human activities have greatly disturbed the biogeochemical cycling of N.

### 1.4.2 N fertiliser

In addition to the cultivation of leguminous crops, another human activity that dramatically affects the global N cycle is increased N input from synthetic fertilisers (Smil 2004). N fertiliser synthesised through the Haber process, converts atmospheric N to $NH_3$ by reaction with $H_2$ based on following equations. The Haber process is an artificial N fixation process and is mainly used to produce fertiliser today. The Haber process converts atmospheric $N_2$ (from the air) to ammonia by reaction with hydrogen (mainly from natural gas) using a metal catalyst under high temperature and pressure. The reaction is reversible, and the production of ammonia is exothermic.

$$\begin{aligned} 3CH_4 + 6H_2O &= 3CO_2 + 12H_2 \\ 4N_2 + 12H_2 &= 8NH_3 \end{aligned} \tag{1.1}$$

The overall application rate of both straight (single nutrient) and compound (multi-nutrient) N applied to grassland and arable changes according to meteorological and economic factors. Generally, the amount of N fertiliser input is estimated according to an average application rate multiplied by the area of arable and grassland. Although N fertiliser can improve crop production, excessive application of synthetic fertilisers increases the loss of $NH_3$ from agricultural land, which is then deposited and reenters biogeochemical cycle (Hesterberg et al. 1996). Erisman et al. (2007) have estimated that approximately half of the annual application of N fertiliser to global agricultural lands is lost to the atmosphere (through $NH_3$ volatilisation and denitrification) and water runoff (nitrate leaching).

### 1.4.3 N deposition

N deposition describes the transfer of Nr from the atmosphere to the biosphere (including the soil). It is a consequence of total emissions of oxidised N from fossil fuel combustion, volatilisation of $NH_3$, denitrification and $NH_3$ emissions from livestock manure. Dry deposition and wet deposition are two major processes in N deposition and are responsible for 70% - 80% of total N emissions deposited to land and ocean (Goulding et al. 1998; Galloway et al. 2004), the remainder emission is still in the atmosphere. Dry deposition is the process through which particles or gases (including $NH_4^+$, $NO_3^-$, $NH_3$, $HNO_3$, $HNO_2$, and NOx) settle out of the atmosphere under gravity. Wet deposition is the process by which atmospheric N (including $NH_4^+$-N, $NO_3^-$-N and Dissolved organic N) accumulates in rain, snow or fog droplets and is subsequently deposited on land or ocean.

Rain gauge and automated wet-deposition samplers are the common instruments used to measure wet deposition. Samples (rain, snow and fog) are usually collected on an event basis either manually or using an automated wet-deposition sampler. Dry deposition is related to land use surface area and different land uses are associated with different N deposition rates. For this reason, it is difficult to measure the flux of dry deposition. As a result, the micrometeorological or inferential method is used to measure the rate of N dry deposition (Fowler et al. 2001; Wesely and Hicks 2000). Of these, the inferential method is considered the best technique for estimating dry deposition when adequate data are available. The inferential method calculated the dry-deposition fluxes to the ecosystem based on measurements of atmospheric concentration of N, the deposition velocities of N, meteorological condi-

tions, surface area and the physical characteristics of surfaces. However, this method is costly to implement at multiple sites. Some previous studies have attempted to quantify N deposition in Europe (Erisman et al. 2015; Fowler et al. 2004). According to Erisman et al. (2015), the rate of N deposition in areas of high dairy and industry development in Europe was 2.5 tonnes N/km$^2$/yr in 1990 and the average deposition value across Europe has decreased from 1990 to 2015. For the UK, Fowler et al. (2004) showed that the highest N deposition rates were 1.2 tonnes N/km$^2$/yr in 1990 and total N deposition in the UK has decreased from 1990 to 2000. From 2004, the UK has had national N deposition networks, which are useful for tracking the spatial distribution and long-term trends of atmospheric N deposition. In the absence of N deposition data (e.g. prior to 2004), the relationship between emissions and deposition is assumed to be constant with time and, prior to 2004, emissions data were used to estimate N deposition (Worrall et al. 2016a).

N deposition can remove Nr from the atmosphere, reducing the risk of forming secondary gas and particulate matter (PM2.5) that can be harmful to human health (Lelieveld et al. 2015). However, too much N deposition has negative impacts on the environment due to acid deposition resulting from NOx cause soil acidification and accumulation of excess nutrients. The atmospheric N deposition to the terrestrial ecosystem can lead to pronounced soil acidification, resulting in a net decrease in soil pH and acid neutralisation capacity (Erisman et al. 2015). When nitrous gas is deposited to the terrestrial biosphere, the NHx can be nitrified, generating nitric acid (Erisman et al. 2015). Several studies have attempted to define the 'critical load' or level of deposition that can cause changes in ecosystem properties (including nitrifi-

cation, leaching, and acidification). For instance, Pardo et al. (2011) and Liu et al. (2011) investigated several ecosystems (e.g. terrestrial and freshwater ecosystems) and both studies found a critical load of N deposition of 0.1 tonnes N/km$^2$/yr, which means the ecosystem impacts are noticeable at an N deposition rate of 0.1 tonnes N/km$^2$/yr or above. Once the N deposition rate surpasses the critical load, the forest will decline. (Savva and Berninger 2010). Excessive N deposited on the land can decrease soil pH (acid deposition) and increase nitrification rate thereby decreasing soil C/N and increasing fluvial N leaching (Corre et al. 2010). Approximately 23% of N deposited on the land is lost to rivers which can cause eutrophication (Howarth 1998; Van Breemen et al. 2002).The OECD(Organisation for Economic Co-operation and Development) defines the eutrophic process as "eutrophication is an enrichment of water by nutrient salts that causes structural changes to the ecosystems such as: increased production of algae and aquatic plants, depletion of fish species, general deterioration of water quality and other effects that reduce and preclude use" (OECD 2003). Eutrophication results when N exceeds the capacity of the water body (e.g., lake, river or sea) to consume nutrients derived from fertiliser use, discharge of wastewater to water bodies, or other sources. In addition, the main ecological impacts of N on marine and freshwater ecosystems are: 1. the abundance of organic particulates (e.g., bacteria, fungi) that impact turbidity and colouration of the water (accelerating corrosion and limiting the flow rate); 2. abundance of inorganic chemicals such as ammonia and nitrites that in the drinking water treatment plants induce the formation of harmful substances such as nitrosamines; 3. reduction of oxygen concentration; 4. potential growth of toxic algae populations

(Collingwood 1977). Thus, N deposition has become an important source of water pollution.

### 1.4.4 Food and feed transfer

Food and feed transfer can be considered as either a net N import or net N export from a terrestrial system (of human food and animal feed) depending on the status of the country (net exporter or importer) (Boyer et al. 2002). As an important N source, the N flux of food and feed transfer was decided by human and animal demand relative to production within the region. If food production can meet the demand of human and animal, the extra food would export to other parts. Conversely, if food production can not meet the demand of people and human, this area would import food and feed. Howarth et al. (1996) estimated that food and feed import comprises 28% of total N input in the northeastern U.S. As a net importer of food and feed, food import in the UK has increased since 1990 and is expected to constitute 21% of total N input by 2020 (Worrall et al. 2016a). In a study of net import of food and feed for the eastern U.S., Boyer et al. (2002) found the highest net import of N in food and feed in more populated catchments. Human sewage outputs to surface waters and livestock manure are also important considerations in food and feed transfer estimates (Galloway et al. 2003). Human sewage N is lost to surface waters or volatilised to the atmosphere during wastewater treatment and livestock manure can be volatilised and lost to the atmosphere as $NH_3$ or lost to surface waters as nitrate, ammonium, nitrite, DON and PON (Schlesinger 2009). Thus, N from food and feed enters the global biogeochemical N cycle via human sewage

and livestock manure. With respect to food and feed transfer at the national scale, Worrall et al. (2009) used commodity trade data to estimate the UK's net N import. This methodology is only suitable at the catchment or national scale when trade data are available (Worrall et al. 2009). Lord et al. (2002) used N surplus method, which defined as the difference between N import to and export from each category to estimate net N surplus for crops, livestock and human. The N surplus can be used to calculate the food and feed transfer when trade data are not available.

### 1.4.5 Atmospheric emission

Atmospheric emissions include $NH_3$ volatilisation, NO, $NO_2$ and $N_2O$ losses via denitrification or fossil fuels. The denitrification to $N_2$ was not accounted in this part and accounted in the part of $N_2$ emission from terrestrial denitrification. The majority of NOx (NO, $NO_2$ and $N_2O$) comes from fossil fuel combustion (including power stations, motor vehicles, and industrial/domestic combustion). Some N compounds are derived from the fuel itself, however, most are formed during fossil fuel combustion from the reaction of atmospheric oxygen and N (Marufu et al. 2004). In addition, NO, $N_2O$ and $N_2$ (not considered in this pathway) are produced by nitrification and denitrification in the soil (Firestone and Davidson 1989). Galloway et al. (2004) estimated that fossil combustion global produces approximately 2.5 $\times 10^1 0$ tonnes of NOx in early 1990 and predicted increase to 5.2 $\times 10^1 0$ tonnes of NOx in 2050. The UK emitting 2.2 $\times 10^7$ tonnes of NOx each year and NOx emission data of UK reveals a decreasing slowly due to emission control strategies for stationary and mobile source are offset by increasing number of vehicles. In the troposphere, $NO_2$

can be dissociated by UV light into NO and an O radical with the latter combining with atmospheric $O_2$ to produce ozone ($O_3$) (Warneck 1999). Elevated $O_3$ near urban areas is thus linked to the amount of NOx emissions (Olszyna et al. 1994). In addition, NOx emissions contribute to total N deposition where $NO_2$ is oxidised to nitric acid and absorbed on the contact surface (soil and vegetation) or dissolved in snow, rain and fog and deposited on land. Thus, the emission of NOx enters the global biogeochemical N cycle again.

$NH_3$ is also an important component of N atmospheric emission and most $NH_3$ originates from agriculture (manures, slurries and fertiliser application). A small portion of $NH_3$ emissions are derived from non-agriculture sources (e.g. sewage works, composting of organic materials and combustion) (Sutton et al. 2000). $NH_3$ contributes to the formation of particulate aerosols in the atmosphere, which is an important air pollutant. The ammonium nitrate and ammonium sulfate was a major part of aerosols which created by $NH_3$ dissolution then react with acid pollutants ($SO_2$ and NOx) in the atmosphere. (Behera and Sharma 2011). The $NH_3$ dissolve and produce the $NH_4^+$ in the atmosphere which is either contained in the particulate matter or dissolved in the rain and deposited to land and surface water. The deposition of $NH_3$ on land or ocean is a major cause of soil acidification and surface water eutrophication, respectively (Sutton et al. 1993; Ferm 1998). The reason about the deposition of $NH_3$ can cause soil acidification is that $NH_3$ in the air neutralises acids when reacting with $H^+$ to form ammonium particles, when this $NH_4^+$ is later taken up by a root, an $H^+$ ion is released from the root and nitrification, acidifying the soil (Binkley and Richter 1987). Globally $NH_3$ emitted

to the atmosphere from terrestrial sources was estimated to be 4.44 $\times 10^7$ tonnes N-$NH_3$/yr in 2001 of which 75% was derived from agriculture (Sapek 2013). In the UK, Sutton et al. (2000) estimated the total UK $NH_3$ emission to be 2.8 $\times 10^5$ tonnes N/yr in 1996 with 81% of emissions coming from agriculture. The emission trends of $NH_3$ have decreased since peak values in the late 1980s and early 1990s, however, the trend has now flattened (`https://uk-air.defra.gov.uk/`). Under current rising air temperatures, volatilisation of $NH_3$ emissions probably will lead to a future rise in $NH_3$ concentration in the atmosphere due to increased speed of hydrolysis of urea (National Atmospheric Emission Inventory (NAEI), `https://naei.beis.gov.uk/`).In addition, as the PH increases, the ionised $NH_4^+$ is liberated into gaseous NH. Conversely, as the PH increases to a point where $NH_4^+$ cannot exist, and all ammonium is presented as $NH_3$ ammonia. In the 1980s, $NH_3$ emission from the UK accounted for 6% of total European N gas emission (Buijsman et al. 1987). The EU National Emission Ceilings Directive (NECD) protocol required that the UK reach a targeted reduction of 18% of $NH_3$ emission for the period 1990 to 2010, and this target was achieved (European Environment Agency 2011). In terms of different sources of $NH_3$ emission, the biggest source of emission is volatilisation from decomposing livestock waste, the second major source is loss from agricultural plant canopies, and the third biggest source is loss from N fertiliser application (Sutton et al. 1995; Pain et al. 1998). Dry deposition of $NH_3$ primarily occurs proximal to the $NH_3$ emission source, therefore, the spatial variability of $NH_3$ emission sources controls the distribution of dry deposition (Sutton et al. 1998; Dragosits et al. 2002). $NH_3$ has drawn considerable attention as a major source

of atmospheric pollution and, spatial monitoring $NH_3$ emission can help people to understand where $NH_3$ pollution is concentrated (Aneja et al. 2008). Eager (1992) was the first to calculate the $NH_3$ emission inventory for Great Britain at a 5 $km^2$ resolution. In 1995, spatially distributed $NH_3$ emission was estimated for the whole of the UK, including Northern Ireland (Dragosits et al. 1998). Hellsten et al. (2008) improved on the model of Dragosits et al. (1998) and found the highest emission in intensive agricultural areas dominated by livestock farming (dairy cattle, pigs and poultry) in the central and eastern UK. The lowest emission occurred in areas with low agricultural activity (i.e. upland and urban areas). In the study of Hellsten et al. (2008), the $NH_3$ emission from fertiliser contributed 12% of total UK $NH_3$ emission in 2000 with the emissions concentrated in the eastern England (arable farming and fertilised grass).

### 1.4.6 $N_2$ emission from industrial source

N contained in fossil fuels can be volatilised as $NH_3$, NOx and $N_2$. Because atmospheric $N_2$ comprises 78% of the Earth's atmosphere, there are no official records of $N_2$ derived from industrial emissions. In the UK, NAEI records the industrial emission of $NH_3$ and NOx but not industrial $N_2$. Previous studies were aiming to quantify a total N budget, considered atmospheric emission of reactive Nr from industrial sources but those studies did not consider industrial $N_2$ and were not able to identify whether net accumulation or loss was occurring (Worrall et al. 2009; Worrall et al. 2015). Worrall et al. (2016a) later estimated the first total N budget of the UK by including fluxes of $N_2$ from industrial sources and concluded that the

UK was a net source of total N from 1990 to 2012.

### 1.4.7 $N_2$ emission from terrestrial denitrification

Denitrification is one possible fate for soil fixed-nitrogen – facilitating its return to the atmospheric pool of $N_2$ (Sprent 1987), these findings also have been confirmed by Follett and Hatfield (2001) and Anne (2010). $NO_3^-$ and $NO_2^-$ are converted to $N_2O$, NO and $N_2$ in the process of denitrification (Firestone 1982; Goregues et al. 2005). Denitrification occurs when soil bacteria use nitrate for their respiration in the place of oxygen in the air. This process occurs most rapidly in warm, wet soils with an abundance of nitrate (Knowles 1982) according to the following pathway:

$$NO_3^- \rightarrow NO_2^- \rightarrow [NO] \rightarrow N_2O \rightarrow N_2 \tag{1.2}$$

NO is enclosed in brackets as it is not commonly detected as a free intermediate. Previous studies have focused attention on whether NO is a true intermediate or a by-product in the denitrification pathway (Garber and Hollocher 1981; Amundson and Davidson 1990). However, $N_2O$ is an obligatory intermediate.

The process of denitrification is widespread in terrestrial ecosystems, especially those in which organic C and nitrate are readily available (Wagner et al. 1996; Wolf and Russow 2000). However, the denitrification rate and flux of $N_2O$ and $N_2$ vary greatly between different land uses (Barton et al. 1999). Denitrification is controlled by the complex interaction between diverse environmental physical, chemical and biological factors (temperature, pH, texture, soil organic carbon, vegetation, soil inorganic N, soil water status, soil aeration) (Wijler and Delwiche 1954; Sirivedhin and Gray 2006). Due to the high background $N_2$ concentration of the atmosphere, mea-

suring denitrification in the field is problematic, and only viable in sealed microbial or biochemical laboratory studies (Burton and Beauchamp 1984). Denitrification is considered the most poorly quantified part of the N cycle (Firestone 1982); limited studies have focused on the denitrification flux from different land uses (Barton et al. 1999). Without high quality denitrification flux data, most studies either do not consider denitrification at all (e.g. Parfitt et al. 2008; Sutton et al. 2011) or crudely estimate denitrification as the difference between N input and output (Ti et al. 2012; Billen et al. 2012).

### 1.4.8 Fluvial N loss (including N loss to groundwater and direct N loss )

Nitrate is primarily the form of nitrogen that is leached. Nitrate is very mobile and is easily moved by water. Other forms of nitrogen, such as ammonium, generally do not leach. Unlike nitrate, the ammonium is attached to the soil and resists movement with water. Nitrate is one of the most common pollutants in surface water and groundwater and is a serious environmental concern (Burt et al. 2011). N fertiliser use and organic manure input are major sources of available nitrate in the soil which is vulnerable to leaching as soils do not absorb the excess N (Goulding et al. 2000). Boyer et al. (2006) and Mulholland et al. (2008) estimated that 10-25% of total N input is exported from soil to surface water. According to a 2018 Environmental Agency report (https://www.gov.uk), 75% of UK rivers were still not in compliance with Water Framework Directive standards. High nitrogen input to rivers is not confined to the UK with many rivers polluted by increased nitrogen

loads across the globe such as the Mississippi river in the USA (Turner and Rabalais 1991; Goolsby et al. 2000) and Changjiang river in China (Yan et al. 2010).

Nitrate sources for river are classified into two types, point and non-point source pollution (Puckett 1994). Point source N pollution refers to N entering a waterway from a single, identifiable source such as a sewage treatment plant, livestock farm, slurry lagoons, or industry. Conversely, non-point sources refer to N from fertiliser, runoff and animal manure (Puckett 1994). Although in the UK lowland rivers close to urban areas, receive large quantities of N from sewage effluent, research has confirmed that agriculture is the main source of nitrate to UK rivers (e.g.Burt and Johnes 1997).

Isotopic and modelling techniques are commonly used to identify N source and transfer between terrestrial and aquatic ecosystems (Ryabenko 2013; Worrall et al. 2012a). Mayer et al. (2002) used N and oxygen isotope ratios of nitrate to estimate the N source of riverine nitrate in 16 watersheds in the northeastern U.S. Seitzinger and Kroeze (1998) and Seitzinger et al. (2005) used a river N export model to estimate fluvial N loss to surface water and found 75% of fluvial N flux from anthropogenic activities. For the UK, the Harmonised Monitoring Scheme (HMS) is a long term river water quality monitoring scheme, which provides data on the water quality at the tidal limit of UK rivers involving routine monitoring at 214 sites in England and Wales, and 56 sites in Scotland. Neal and Davies (2003) used the data from HMS to estimate the fluxes of N species for eastern UK rivers. Furthermore, Worrall et al. (2012a) also used HMS data to estimate N export for the UK which describes the fluvial N flux in different land use and soil types.

In addition to the fluvial flux of N from the tidal limit, N flux to groundwater is another important N output pathway (Worrall et al. 2012a). Nitrate can be leached from rivers to groundwater or directly recharged to groundwater through soils. N concentrations have increased in some UK groundwater(Stuart et al. 2007). Sources of N in groundwater include fertiliser, animal waste, and domestic (human)/industrial waste. High N concentration in groundwater is considered detrimental to human health (quality of drinking water) (Majumdar and Gupta 2000). The 1980 European Drinking Water Directive (EEC/80/778) relating to the quality of water intended for human consumption set a 50 mg/L limit for nitrate in groundwater that the UK adopted in 1989 (The Water Supply Regulations 1989). In the UK, groundwater nitrate concentrations exceed this limit in many areas with the highest nitrate concentration observed in the Chalk of East Anglia and Humberside and the Permo-Triassic Sandstone of Staffordshire (Rivett et al. 2007). Several studies have focused attention on nitrate concentrations in groundwater and highlighted the need to manage levels through groundwater treatment (Rivett et al. 2007; Stuart et al. 2007). Using unpublished Environment Agency monitoring data, Rivett et al. (2007) mapped the mean nitrate concentration across England and Wales. The study of Rivett et al. (2007) observed that elevated nitrate concentrations were widespread and continuing to rise across England and Wales. Stuart et al. (2007) used a statistical technique to model long-term trends of N concentration across the UK, revealing a significant increase in nitrate concentration in UK groundwater over the last decade. According to Stuart et al. (2007), UK groundwater nitrate concentration increased on average by 1 mg N/l per year since 1990, resulting in an

additional 3 $\times 10^5$ tonnes of net N storage in groundwater. Furthermore, Howden and Burt (2009) demonstrated the evidence for hydrogeological controls on trends in nitrate concentrations in west England.

## 1.5 Nitrogen Budget

### 1.5.1 Introduction to nitrogen budget

According to Leip et al. (2011), " *a nitrogen budget consists of the quantification of all major nitrogen flows across all sectors and media within given boundaries, and flows across these boundaries, in a given time frame (typically one year), as well as the changes of nitrogen stocks within the respective supra-national level (i.e. Europe), sub-national level (regions, districts), for watersheds or even individual households or for economic entities (i.e. farms)*". An N budget is estimated as the difference between total N input and N output (Kremer 2013). The N budget can represent an indicator of N accumulation or depletion in the terrestrial biosphere (Kremer 2013). Accumulation status of an N budget is an indicator of potential risk of N to the environment (N emission to atmosphere and N runoff to water). The depletion status of an N budget refers to the potential risk of a decline in soil fertility which may lead to soil related problems such as soil erosion (lower N causes soil compaction and increase soil erosion) and a decrease in agricultural production. To understand the status of an N budget, all possible N pathways should be considered. However, this proves difficult in practice due to data availability constraints and thus most studies (e.g.Howarth et al. 1996; Ti et al. 2012; Worrall et al. 2015) do not account

for all N pathways.

### 1.5.2 Literature on N budgets at different scales

The N biological cycle was affected by many factors such as land use, climate change, hydrology and human activities which made the N cycle are complicated. The N environmental pollution (e.g. acid rain, greenhouse gas emissions, river water pollution) not occur at the source of N, and N pollution travel to other areas far from the N source. (Puckett 1994). According to Kimura et al. (2009), the environmental impact is partially determined by N pathways which will change depending on scale. Therefore, analysing the N budget at a regional scale is quite helpful for understanding N cycle mechanisms, improving the modelling of N movement through the environment, and managing N pollution.

Howarth et al. (1996) estimated a total N budget and riverine N flux to the North Atlantic Ocean for 14 regions in North America, South America, Europe and Africa. In this study, non-point sources of N dominated riverine fluxes to the ocean. In all regions, total river N flux was correlated with anthropogenic N input including N fertiliser, N deposition caused by human activity, fixation by leguminous crops, and the import of agricultural products (food and feed). All data used to calculate the different N pathways flux come from literature and measurement. Specifically, N fertiliser input was calculated by the N fertiliser application rate multiplied by the areas of fertiliser applied within catchment, the N deposition was calculated by the deposition rate (wet deposition and dry deposition) multiplied area of each catchment, N fixation was derived by multiplying the rate of fixation for each crop type

by the crop areas within catchment, and net import or export of N in agricultural products was estimated by FAO statistics on per country imports and exports of products, and per country values were scaled by catchment areas. On average, 25% of the total N input from anthropogenic sources is lost to river systems (Howarth et al. 1996). Galloway et al. (2004) constructed regional N budgets for Africa, Asia, Europe/Former Soviet Union (FSU), Latin America, North America and Oceania and calculated the major N flux of each region (Table 1.1). Natural BNF was the dominant Nr source in Africa, Latin America and Asia and anthropogenic Nr production (e.g. from fertiliser and cultivation-induced BNF) was the dominant Nr source in Asia and Europe/FSU. For N output, riverine N export of Asia was highest in the world which causes more N loss to rivers and higher risk for eutrophication in Asian water compared to other regions in the world (Galloway et al. 2004). Denitrification and Nr storage contribute the largest uncertainties in an N budget (Barton et al. 1999), highlighting the need for improved understanding of these pathways in the future.

**Table 1.1:** Reactive nitrogen creation by region ($10^6$ tonnes N/yr). *Source: From Galloway et al. (2004).*

| Nr | Pathway | Africa | Asia | Europe/FSU | L.America | N.America | Oceania |
|---|---|---|---|---|---|---|---|
| Nr input | Fixation in lighting | 1.4 | 1.2 | 0.1 | 1.4 | 0.2 | 0.2 |
| | BNF | 25.9 | 21.4 | 14.8 | 26.5 | 11.9 | 6.5 |
| | fertiliser | 2.5 | 40.1 | 21.6 | 3.2 | 18.3 | 0.4 |
| | Cultivation BNF | 1.8 | 13.7 | 3.9 | 5.0 | 6.0 | 1.1 |
| | Food and feed import | 1.2 | 13.8 | 9.6 | 2.5 | 5.0 | 0.6 |
| | Fossil fuel | 0.8 | 5.7 | 6.1 | 1.3 | 7.3 | 0.4 |
| Nr output | Food and feed export | 1.1 | 5.1 | 15.2 | 2.7 | 8.3 | 0.3 |
| | Atmospheric NOx | 1.9 | 1.9 | 3.0 | 2.3 | 3.8 | 0.6 |
| | Atmospheric NHx | 1.4 | 1.4 | 2.4 | 2.0 | 0.6 | 0.5 |
| | Fluvial N loss | 8.5 | 21.8 | 9.1 | 9.7 | 7.8 | 2.1 |

At the country scale, recent studies have included N budgets for China (Ti et al. 2012); Brazil (Filoso et al. 2006); South Korea (Bashkin et al. 2002); New Zealand (Parfitt et al. 2006). Bashkin et al. (2002) constructed an N budget for South Korea revealing that South Korea acts as an N sink (total N inputs larger than total N outputs). In the 1990s, over 50% of N input in South Korea was imported from abroad. During 1994-1997, fertiliser was the largest N input (accounting for 55% of the total N input) and the dominant N outputs were attributed to $NH_3$ volatilisation (18%), biological denitrification (16%) and river discharge (23%). Excessive N introduced through human activity has led to pollution and eutrophication of the Yellow Sea (Bashkin et al. 2002). Ti et al. (2012) estimated N input and output for mainland China. According to Ti et al. (2012), total N inputs increased from 0.6 tonnes N/km$^2$/yr in 1985 to 51 tonnes N/km$^2$/yr in 2007. Due to the high population in China, N fertiliser was observed to be the dominant N input with an increase observed over the 22 years of the study (Ti et al. 2012). In 2007, N fertiliser accounted for 54% of total N input and more than half of the total N input was denitrified or stored in the system. $NH_3$ volatilisation accounted for 19-23% of total input and 18-20% of total input was exported to surface water. Filoso et al. (2006) estimated the N budget of Brazil to advance understanding of the N cycle and impacts of anthropogenic activities in the world's largest tropical country. N inputs to Brazil from human activities doubled from 1995 to 2002, and associated with BNF cultivation of leguminous crop represents one-third of anthropogenic N inputs. The first N budget for New Zealand was estimated by Parfitt et al. (2006). The average national N inputs were estimated to be 3.7 tonnes N /km$^2$/yr and are mainly from

BNF. The national N output was estimated at 4.1 tonnes N/km$^2$, and the relative contribution of N outputs listed in order of decreasing importance was N leaching >$NH_3$ volatilisation >equal contributions from exports of produce, denitrification N and loss of N by erosion.

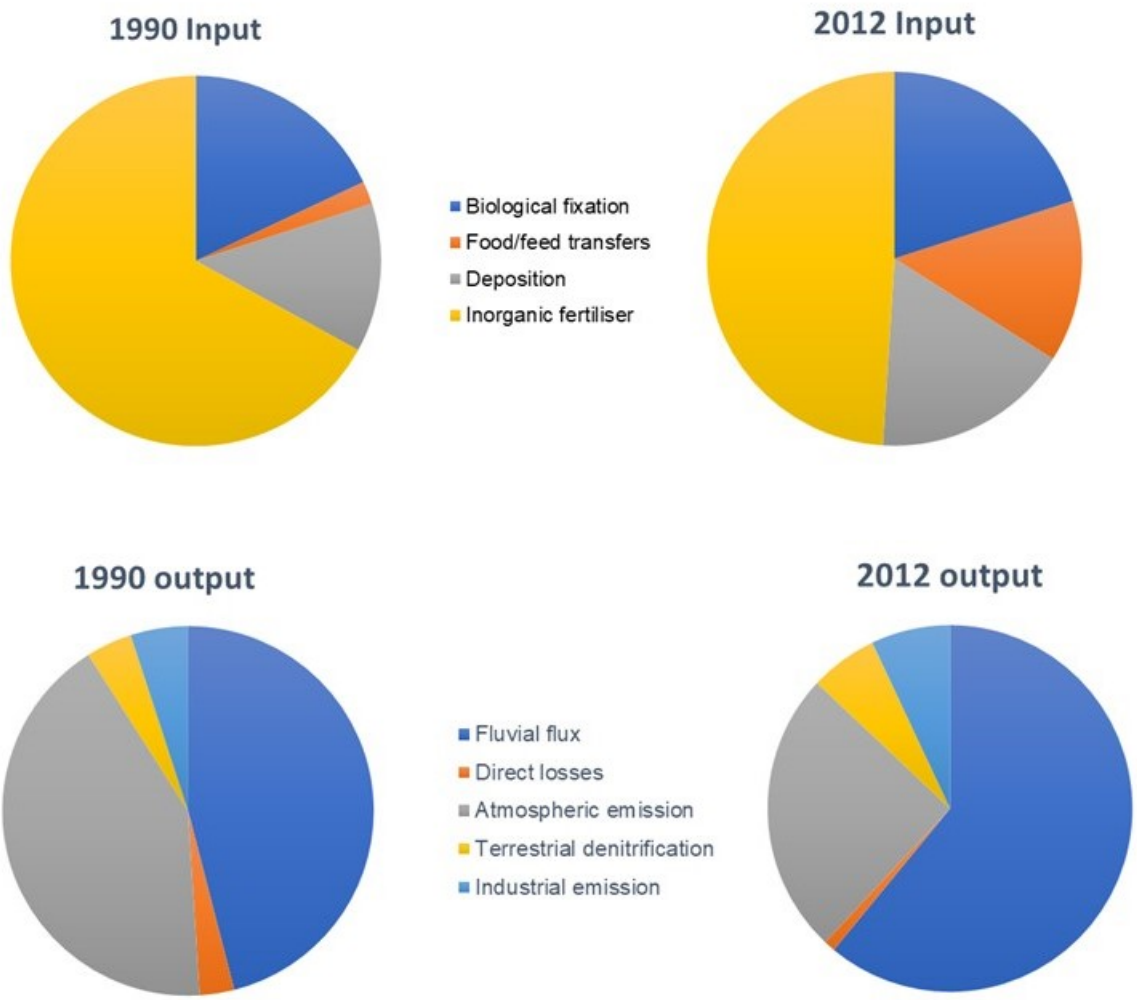


**Figure 1.4:** Proportion of input and output in 1990 and 2012 for the UK. *Source: From Worrall et al. (2016a).*

For the UK, Worrall et al. (2016a) estimated the total N budget from 1990 to 2012 and predicted fluxes in 2020. The N flux for each pathway is summarized

in Table 1.2 and Table 1.3 and the proportion of total input and output in 1990 compared to 2012 is shown in Figure 1.4. The study found that total N budget for the UK was negative (inputs <outputs) but by 2031 would be positive (inputs >output). Fertiliser was the biggest N input in the UK but declined in use over 1990 to 2020 with atmospheric deposition and food and feed imports increasing. The dominant N output was fluvial N losses at the soil source which means N loss from soil to river (46-61% of total N output) and all N pathways of total N output decreased except atmospheric emission and denitrification (Worrall et al. 2016a).

Studies of N budgets at the catchment scale can aid understanding of the N cycle within a catchment and N loss to the river or the ocean. Boyer et al. (2002) described N input and output for 16 catchments of the northeastern U.S. Over the combined areas of 16 catchments, N deposition was the largest N input, accounting for 31% of the total input, followed by N transfer in food and feed (25%), fixation in agricultural lands (24%), N fertiliser (15%), BNF in forests (5%), and 25% of total N input was exported to river system (Boyer et al. 2002 ). In the study of Boyer et al. (2002), because N input was related to land use, N input varies widely by catchment. According to Boyer et al. (2002), N deposition was the largest source within a forested basin whilst N transfer in food and feed was the largest source in urban areas. Yan et al. (2003) estimated N input, output and balance for the Changjiang river basin in China for the period 1968 – 1997. The total N input of Changjiang river basin showed an increase over this period: total N input in 1997 was threefold greater than 1968 levels. Before 1977, BNF was the biggest N input, but from 1983 onwards, this was superseded by N fertiliser (Yan et al. 2003). The

N input exported to rivers in the Changjiang basin increased over a 30-year period by 30%. Overall, in the Changjiang basin, N fertiliser, human population density, and manure N production were good predictors of the river's nitrate concentration and flux. Sobota et al. (2009) quantified N inputs and outputs for 23 watersheds in California U.S. to analyse how climate, hydrology and land use influenced watershed N export. The total N inputs ranged from 0.6 to 11.2 tonnes N/km$^2$/yr and 80% of total N input were from agricultural sources. Climate and anthropogenic N inputs were the major factors influencing seasonal variances N export in California.

Few research studies have focused on calculating a N budget for the UK (e.g.Worrall et al. 2009; Worrall et al. 2016a). These studies analysed characteristics of N cycling and N pollution in the environment based on N budgets at the catchment-scale. Specifically, nitrate concentration and flux were estimated in the River Thames (Howden et al. 2010), N pollution in farmed regions (Howden et al. 2011b), nitrate pollution in the Alton Pancras catchment (Howden et al. 2011a), a River Thames total N budget model (Howden et al. 2013) and N modeled across spatial scales in the UK (Greene et al. 2015). Worrall et al. (2015) estimated the N budget of the river Thames catchment and observed that the catchment had accumulated 3.2 $\times 10^5$ tonnes N at a rate of 5.5 tonnes N/km$^2$/yr over 35 years since 1973. In the Thames catchment, net N in food and feed transfer was identified as the dominant N input and fluvial loss at the soil source (N loss from soil to river) was the dominant output (Worrall et al. 2015).

## 1.6 Aims and objectives of the thesis

This study fills existing knowledge gaps (e.g., previous studies failed to consider industrial $N_2$) by determining the flux of all N pathways and the distribution of N flux associated with each pathway according to land use and soil type. Together, this data contributes to the spatially-differentiated total N budget that considers a comprehensive list of N inputs (biological N fixation, atmospheric N deposition, food and feed transfer, and inorganic fertiliser application) and outputs (atmospheric N emission, terrestrial denitrification, N fluvial flux loss from the soil, gas emissions from sewage treatment plants, direct N sewage flux loss, and groundwater loss). The new spatially differentiated N budgets will improve understanding of N fluxes through the environment, the changing pattern in N inputs and outputs, the mechanisms for N movement through the environment, impact factors (e.g. land use, soil type and climate), and the anthropogenic N problem. This investigation aims to provide scientific evidence for controlling N loss as a basis for managing N losses and strategies for managing N pollution. This aim will be accomplished by addressing the following research objectives:

1. To compile a spatially-differentiated total N budget at 1 $km^2$ scale for GB that considers total N inputs and outputs (Land use, soil type, and annual N flux data were of limited availability in Northern Ireland but were available for GB, therefore, this study developed the spatial total N budget for GB only).

2. To identify areas of N accumulation and loss across the Trent catchment.

3. To test in the field where N accumulation is occurring.

4. To analyse N accumulation and N budget trends through time (The Trent catchment has very long records of surface and ground water quality that can be used to optimise understanding of N flux and where N is accumulating).

5. To reveal the spatial heterogeneity of the total N budget and quantitatively analyse the contribution of different factors to the observed N spatial patterns change within a catchment.

6. To evaluate the factors that influence nitrate flux to the surface water and provide strategies to reduce N loss in England.

## 1.7 Thesis content and organisation

Chapter 1 presents the background of this study and provides an overview of bio-geochemical N cycling through a literature review of different N pathways and N budgets at different spatial and temporal scales. It also identifies key knowledge gaps.

Chapter 2 addresses a gap in the existing literature by constructing the first N budget at 1 $km^2$ scale for GB including all significant N input and output pathways. The new budget provides an up-to-date and accurate reflection of the processes contributing to the distribution of sink and source areas across GB. The chapter also discusses the relationship between the N budget and current distribution of land use across GB, exploring how future land use changes may influence the N budget.

Chapter 3 presents a spatially distributed N budget for the Trent catchment

based on primary and secondary data (BNF, N deposition, fertiliser, N gas emissions and denitrification). Characteristics of the Trent catchment, the selection criteria for soil sampling sites, the laboratory methodology, and the results of the investigation (e.g. with areas of N accumulation identified) are presented.

Chapter 4 presents an N budget time series for the Trent catchment based on primary data and secondary data. Changes in the spatial N budget through time are predicted. The chapter also provides a quantitative analysis of different factors contributing to the Trent catchment N budget and evaluates how agricultural environmental risk might be decreased through improved N source management practices.

In Chapter 5, water quality monitoring data (nitrate concentration and river discharge) are collated for England from 2005 to 2016 and applied to reveal factors (catchment characteristics and hydroclimatic characteristics) contributing to nitrate pollution in surface water. This chapter also discusses N flux factors (e.g. land use, soil types) and their relative importance on the N budget.

Finally, Chapter 6 is the concluding chapter, providing an overall summary, discussion of the limitations of the research, and suggestions for future work.

**Table 1.2:** The N flux of each input and output for 1990 - 2001. *Source: From Worrall et al. (2016a).*

| year | N inputs ($10^3 tonnes N/yr$) | | | | | N outputs ($10^3 tonnes N/yr$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Deposition | BNF | Food and feed transfers | fertiliser | Nr emission | Industrial $N_2$ | Denitrification to $N_2$ | Fluvial loss | Groundwater sink | Direct discharges |
| 1990 | 298 | 420 | 42 | 1582 | 2115 | 231 | 205 | 2332 | 15 | 135 |
| 1991 | 335 | 420 | 81 | 1515 | 2054 | 241 | 206 | 2318 | 15 | 116 |
| 1992 | 341 | 420 | 102 | 1365 | 2008 | 243 | 205 | 2316 | 15 | 125 |
| 1993 | 302 | 421 | 82 | 1219 | 1901 | 239 | 209 | 2250 | 15 | 109 |
| 1994 | 370 | 415 | 79 | 1248 | 1832 | 240 | 209 | 3053 | 15 | 102 |
| 1995 | 314 | 411 | 82 | 1348 | 1748 | 223 | 209 | 2611 | 15 | 98 |
| 1996 | 337 | 412 | 99 | 1333 | 1686 | 222 | 207 | 2634 | 15 | 85 |
| 1997 | 319 | 416 | 105 | 1441 | 1590 | 217 | 204 | 1961 | 15 | 90 |
| 1998 | 319 | 413 | 90 | 1370 | 1543 | 210 | 203 | 3003 | 15 | 91 |
| 1999 | 308 | 410 | 145 | 1284 | 1463 | 198 | 205 | 2786 | 15 | 84 |
| 2000 | 349 | 406 | 144 | 1268 | 1410 | 192 | 206 | 3470 | 15 | 78 |
| 2001 | 393 | 410 | 254 | 1115 | 1385 | 192 | 208 | 2652 | 15 | 80 |

**Table 1.3:** The N flux of each input and output for 2002 - 2012. *Source: From Worrall et al. (2016a).*

| year | N inputs ($10^3 tonnes N/yr$) | | | | | N outputs ($10^3 tonnes N/yr$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Deposition | BNF | Food and feed transfers | fertiliser | Nr emission | Industrial $N_2$ | Denitrification to $N_2$ | Fluvial loss | Groundwater sink | Direct discharges |
| 2002 | 387 | 411 | 263 | 1197 | 1329 | 184 | 206 | 2409 | 15 | 74 |
| 2003 | 381 | 408 | 174 | 1131 | 1309 | 186 | 207 | 1917 | 15 | 79 |
| 2004 | 373 | 410 | 222 | 1129 | 1278 | 187 | 206 | 2119 | 15 | 66 |
| 2005 | 384 | 409 | 238 | 1118 | 1260 | 186 | 208 | 1657 | 15 | 75 |
| 2006 | 383 | 409 | 254 | 1090 | 1229 | 189 | 208 | 1610 | 15 | 64 |
| 2007 | 378 | 409 | 270 | 1074 | 1177 | 199 | 207 | 2350 | 15 | 68 |
| 2008 | 380 | 407 | 268 | 979 | 1073 | 246 | 205 | 2870 | 15 | 72 |
| 2009 | 381 | 415 | 263 | 997 | 960 | 247 | 205 | 2057 | 15 | 72 |
| 2010 | 380 | 407 | 237 | 1046 | 945 | 278 | 206 | 1650 | 15 | 56 |
| 2011 | 391 | 409 | 248 | 1036 | 899 | 257 | 205 | 1348 | 15 | 50 |
| 2012 | 366 | 413 | 297 | 1017 | 910 | 265 | 203 | 2221 | 15 | 49 |

# Chapter 2

# A spatial total nitrogen budget for Great Britain

## 2.1 Introduction

N comprises approximately 78% of Earth's atmosphere and is a key element of many biogeochemical processes (Galloway et al. 2008). As a basic nutrient element, N can limit the productivity of natural ecosystems. The global N cycle has been strongly influenced by human activity with increasing N fertilizer application and expanding areas of legume cultivation (Fowler et al. 2013). With increasing population and economic growth, human activity introduces additional N into terrestrial ecosystems which far exceeds biologically fixed N (Galloway and Cowling 2002). The extra Nr input to terrestrial ecosystems greatly increases food production but also induces a series of environmental problems including greenhouse-induced global warming via the production of $N_2O$ (Vitousek et al. 1997); ozone layer destruction (Ravishankara et al. 2009; acid rain (Driscoll et al. 2001); and groundwater pollution (Choudhury

and Kennedy 2005).

Anthropogenically-sourced N has disrupted the global N cycle, focusing attention on the need to better manage N inputs and outputs. (Schlesinger 2009; Galloway et al. 2008). The environmental pollution caused by disrupted N cycle has been presented in last chapter. Maintaining the balance between N input and output is essential to ensure the optimal use of this important resource while limiting pollution problems; the N budget has been considered as a priority agri-environment indicator by many countries (OECD 2003). As a result of its importance, several national and regional scale N budget studies have been published for (before the study of Worrall et al. 2016a): the catchment area of the North Atlantic Ocean (Galloway et al. 2004); the Republic of Korea (Bashkin et al. 2002); Canada (Janzen et al. 2003); the Netherlands (Kroeze et al. 2003); Brazil (Filoso et al. 2006); New Zealand (Parfitt et al. 2006); Finland (Salo et al. 2007); France (Billen et al. 2012) and China (Ti et al. 2012). Furthermore, several N budget at different systems also presented such as the agricultural land of Asian counties (Shindo 2012); a forested catchment area in New Hampshire, USA (Yanai et al. 2013); forest ecosystems (Johnson and Turner 2014); and grasslands of south-east Scotland (Jones et al. 2017). Although these studies have contributed to an improved understanding of N pathways, none of these studies have yielded a total N budget for a number of reasons as summarised by Worrall et al. (2016a). Firstly, one major reason for incomplete N budget is the different boundaries used in monitoring studies. In a previous study, Worrall et al. (2015) constructed a N budget for the terrestrial biosphere of the Thames catchment. The boundary of terrestrial biosphere of the Thames

catchment described that the water below the water table and the unsaturated zone of geology of this catchment are not included in the terrestrial biosphere. All industrial $N_2$ emission were assumed to come from geological sources (geosphere), therefore the industrial $N_2$ emission was not consider in this study as it was outsides of the terrestrial biosphere (e.g. Hemond 1983; Worrall et al. 2015). In addition, previous studies have only considered political boundaries rather than hydrological boundaries, thereby, excluding the fluvial N loss from transboundary rivers (Ti et al. 2012). Secondly, it is problematic to quantify $N_2$ as the dominant end product of denitrification due to the high background concentration of naturally occurring atmospheric $N_2$ (Groffman et al. 2006). For this reason, N budgets often include only Nr species that comprise all N species other than $N_2$ and, therefore, cannot be considered 'total' N budgets. Kroeze et al. (2003) estimated an Nr sink of 469 $\times 10^3$ tonnes N/yr for the entire Netherlands. Kroeze et al. (2003) assumed total N input equal to output based on a mass balance model, the difference between N inputs and outputs was assumed to be denitrification $N_2$. Nr sink was balanced by denitrification to $N_2$. Therefore, the amount of denitrification to $N_2$ was also estimated to be 469 $\times 10^3$ tonnes N. Thirdly, several studies calculate N budgets based on a single year of data rather than multiple years, and therefore may not reflect actual processes but changes in legacy stores and sinks (i.e. due to N reserves and reservoirs having different time constants (Addiscott 1988)).

Previous studies (e.g. Galloway et al. 2004; Worrall et al. 2009; Worrall et al. 2015) have calculated the N budget based on Nr alone, which has been justified since excess Nr can affect the environment quickly. However, to fully understand how N

cycles through the environment, a total N budget that includes Nr and $N_2$ is critical. Worrall et al. (2016a) calculated the UK National scale total N budget by including industrial emissions of $N_2$ as well as both terrestrial and aquatic denitrification to give the total N budget at the national scale. The total N budget for the UK was estimated to have declined from -1941 $\times 10^3$ tonnes N/year in 1990 to -1446 $\times 10^3$ tonnes N/year in 2012, which means that the UK was a net source of total N to its external environment (atmosphere and surrounding seas). The magnitude of this source has declined since 1990 and was expected to decline until at least 2020. Although the Worrall study (Worrall et al. 2016a) is important for providing the first total N budget for a country, a key limitation was that the total N budget was not spatially-distributed. Other studies ( Lord et al. 2002; Bouwman et al. 2005; Ti et al. 2012) have developed spatially-differentiated Nr budgets, but have not calculated a spatially-differentiated total N budget. Most of previous studies (Galloway et al. 2004; Worrall et al. 2009; Worrall et al. 2015) have just focused on reactive N budgets (without account for the spatial variability) and when studies have considered the catchment or country as a single entity which only showed the N surplus or deficit at individual catchment level and at national level. However, in many countries, N surplus or deficit per hectare of terrestrial biosphere can be highly variable, meaning that some sub-regions could be severely affected by excessive N and others not. Therefore, the spatial N budget has the potential to be a more powerful N balance indicator than a national level N budget. In addition, previous spatial N budget studies (Ti et al. 2012; Bouwman et al. 2005; Lord et al. 2002) did not include all N pathways (excluding $N_2$) and were, therefore, incomplete. This

chapter fills this gap by constructing a spatial N budget across GB that not only includes flux via significant N pathways but differentiate these according to land use and soil type. This chapter is also the first to produce a spatially-differentiated total N budget that considers a comprehensive list of N inputs (BNF, atmospheric deposition, food and feed transfer, and inorganic synthetic fertilizer) and outputs (atmospheric emission, terrestrial denitrification, fluvial flux loss from the soil, gas emissions from sewage treatment plants, direct sewage flux loss, and groundwater loss). The outcome of this chapter will permit identification of the N status (sink or source) of different land uses and enable assessment of how land use change might impact the N budget of GB.

## 2.2 Approach & Methodology

### 2.2.1 Data and study area

GB is an ideal place to construct a spatial total N budget. Firstly, according to Worrall et al. (2009), GB is a hotspot for fluvial N flux and the export of dissolved N from GB (varied from 1.1 to 3.1 tonnes N/ha/yr) is higher than export in any other region of the same size of Europe during the period from 1974 to 2005. Secondly, it has already been demonstrated that there are detailed records of N inputs and outputs for GB (Bell et al. 2011; Worrall et al. 2016a).

Due to the availability of land use and soil type data across GB (England, Scotland and Wales) but limited availability elsewhere in the UK (i.e. Northern Ireland), the present study developed the first spatial total N budget at a 1 $km^2$ grid scale

for GB only. The 1 $km^2$ was the smallest scale spatial scale for which data were available in GB. The quality of the individual measurement data varied and so this study attempted to assess the uncertainty in each input or output. Most of the nitrogen fluxes needed for a complete N budget were derived from government and published data sources. This thesis used the error estimation provided by each individual source. Where no error or uncertainty estimate was given, a default value ±80% was used.

### 2.2.2 Methodology

Our GB total N budget was estimated based on the gross N balance methodology (OECD 2003) which calculates all inputs and outputs from each 1 $km^2$ area. The present study examined all significant pathways of N (Figure 2.1). Input pathways considered were: BNF; atmospheric deposition; food and feed import; and inorganic fertilizer application. Output pathways considered were: atmospheric emissions; terrestrial denitrification; food and feed export; fluvial losses from the soil; gas emissions from sewage treatment plants; direct sewage flux; and ground water loss (N loss from soil and river to groundwater). Because GB is a net importer of food and feed, these were considered here as an input pathway (Worrall et al. 2015). The N budget model for GB used was:

$$
\begin{aligned}
N\ budget_{GB} = {} & Inorganic\ fertilizer + Biological\ N\ fixation \\
& + Atmospheric\ deposition + Net\ food\ and\ feed\ transfer \\
& - Atmospheric\ emission - Fluvial\ loss\ at\ soil\ source \\
& - Denitrification\ to\ N_2 - Direct\ N\ loss \\
& - Industrial\ emission - Groundwater\ loss \\
& - Emission\ from\ sewage\ treatment\ plant
\end{aligned}
\tag{2.1}
$$

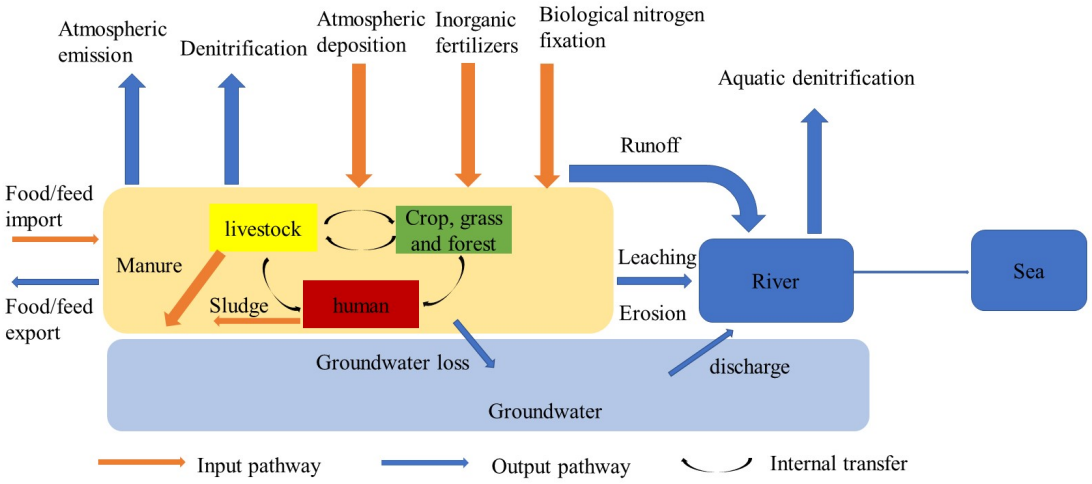


**Figure 2.1:** Flow diagram of total N budget for each 1 km$^2$ gridded area. Orange arrows denote N inputs while blue arrows denote N outputs.

### 2.2.3 N inputs

BNF is a major input of N to land, occurring in both agricultural and natural ecosystems. In GB, the major N fixing crops are legumes (beans, peas) and clover. For agricultural ecosystems, BNF rates were assumed to be 4 tonnes N/km$^2$/yr for beans and peas; and 15 tonnes N/km$^2$/yr for clover (Smil 1999). For agricultural lands, the

land areas of the respective crops were obtained from the June Agricultural Census (Defra 2015a) and the area of each of these crop types from DEFRA was available from 2001 to 2018. Therefore, total BNF in agricultural ecosystems was estimated by scaling the N fixation rate of the identified crops by their areas, respectively. For natural ecosystems (i.e. non-agricultural lands), the UK is divided into classes of forest and grassland and these areas were identified from the Centre for Ecology & Hydrology CEH land cover map (https://www.ceh.ac.uk/services/land-cover-map-2015). N fixation in temperate forests has been well studied (Cleveland et al. 1999) and there is no substantial difference in rates of BNF between coniferous and deciduous forests (Boring et al. 1988). Therefore, in the present study, the rates of N fixation in temperate forests are used as average rates of N fixation for all forests in GB. Forest and grassland BNF rates were obtained from Cleveland et al. (1999), which assumed a constant value of 0.04 tonnes N/km$^2$/yr for forest and 4.70 tonnes N/km$^2$/yr for grass (average value for all kind of grass). An estimated uncertainty in biological N fixation of ±25% (SEM) was calculated from published ranges (Smil 1999; Cleveland et al. 1999; CEH).

Nr (reactive nitrogen) in the atmosphere was mainly derived from fossil fuel combustion, N fertilizer application and agricultural development, 70%-80% Nr in the atmosphere was deposited to the land surface and surface water by dry deposition and wet deposition, whilst the rest of the Nr remained in the atmosphere or was assumed to be transported offshore (Asman 1998; Goulding et al. 1998). Most of Nr emission was assumed to be deposited to the land surface and surface water, previous studies have constructed a relationship between N deposition and atmospheric N

emissions (Asman 1998; Goulding et al. 1998). The relationship between deposition and emission can be used to estimate N deposition when atmospheric N emissions data are available but this relationship was not suitable for distributed assessment at the national scale. For GB, annual atmospheric deposition data has been consistently recorded since 2004 at a 5x5 $km^2$ resolution (CEH: www.ceh.ac.uk). For the purposes of the present study, these data were converted to a 1 $km^2$ grid scale. Specifically, atmospheric deposition at 5x5 $km^2$ resolution are based on a grid-average of multiple land classes. The 5x5 $km^2$ atmospheric deposition data can be added to ArcGIS and divided into 1$km^2$ resolution data by using ArcGIS tool. In ArcGIS, the point data of atmospheric N deposition was created from 5x5 $km^2$ raster data using the point to raster tool. The raster data at 5x5$km^2$ resolution was then converted to polygon data at 5x5 $km^2$ resolution using the Raster to Polygon tool. In order to get the deposition polygon data showed grid-average of multiple land classes at 1$km^2$ resolution (the average deposition value for each 1 $km^2$ grid), a new fishnet and fishnet point at 1 $km^2$ resolution was generated using the create fishnet tool and spatially joined with the polygon deposition data of 1 $km^2$ resolution using the spatial join tool. Before 2004, atmospheric deposition data were reported by Fowler et al. (2005). However, neither the atmospheric deposition data recorded by Fowler et al. (2005) nor CEH include the deposition of dissolved organic nitrogen (DON). Previous studies only reported precipitation DON concentration but provided no estimate of the amount of total wet DON deposition for the UK. However, Moor House National Nature Reserve located in the northern Pennines,UK has recorded annual DON deposition from 1992 which can be used to simulate the DON data

for GB. DON deposition data in Moor House was reported by Worrall et al. (2006) as between 0.01 and 0.15 tonnes N/km$^2$/yr which is small when compared to other compounds of N such as nitrate and ammoniacal N (various from 0.87~4.26 tonnes N/km$^2$/yr). Thus, herein the DON deposition rates measured at Moor House were applied across GB. In addition, it was also possible to estimate the C/N ratio for atmospheric deposition at Moor House to estimate DON deposition from sites where DOC deposition has been recorded. There were 3 sites with recorded DOC deposition data which were also quite small varying from 0.73 to 4.83 tonnes C/km$^2$/yr (Worrall et al. 2006). Given a C/N ratio = 25, the DON deposition would vary from 0.02 to 0.19 tonnes N/km$^2$/yr. Therefore, the total atmospheric N deposition could be estimated for each 1 km$^2$ across GB. The CEH data were not accompanied by an error estimation, an uncertainty of ±80% (SEM)was ascribed as a credible error for atmospheric deposition in this chapter.

For N in food and feed transfers as well as seed and plant transfers, the UK's Defra (Department for Environment, FoodRural Affairs) has recorded trade data in food, feed, and drink including indigeneity and degree of processing, since 1988 (Defra 2015a). The key commodities of the Defra data were: whisky, wine, cheese, poultry meat, poultry meat product, beef, veal, wheat, lamb (mutton), pork, breakfast cereals, milk, cream, bacon, ham, butter, egg, egg product, fresh vegetables, fresh fruit and salmon. The commodity trade data in food, feed and drink can be converted to N trade data by reference to the average N contents of food, feed and drink by means of the Roe et al. (2015) composition of foods integrated dataset (CoFID). Worrall et al. (2015) and Worrall et al. (2016a) used commodity trade

data to estimate the amount of food and feed transfer for the UK, however, this method cannot spatially distribute the amount of food and feed transfer to a 1 $km^2$ resolution. To calculate the amount of food and feed transfer at a 1 $km^2$ resolution, the food and feed transfer can be summarised by into livestock N balance, human N balance, and crop N balance. In this chapter, the livestock N balance and crop N balance were quantified, following the N surplus method used by Lord et al. (2002) who estimated all fluxes of input and output for livestock and crops. The approach of Lord et al. (2002) was used to calculate the N balance for each category of livestock (sheep, cattle, pig and poultry) and crop (crop and non-crop) at a 1 $km^2$ resolution. In addition, the human N balance can be estimated by difference between human demand and human output using the approach of Boyer et al. (2002). The human output was considered as sewage flux which would be accounted for in fluvial loss and gas emission from sewage treatment plants. In this step, the human balance is considered as the input per human. Human input flux was assumed to be entirely due to human N consumption from diet which was from the Food and Agriculture Organization of the United Nations (FAO: http://www.fao.org/home/en/). The N surplus of crop, livestock and human N consumption are only reported within government or published data source. The uncertainty provided by each individual source was accepted. The uncertainty of crop and livestock were estimated to be ±80% (SEM) based on Lord et al. (2002). The uncertainty of human N consumption (±80%,SEM) was provided by the FAO.

The amount of inorganic N fertilizer application in the UK was obtained from the British Survey of Fertilizer Practice which has recorded synthetic inorganic fertilizer

inputs from 1992 to 2015 (British Survey of Fertilizer Practice, 1992~2015). For the period 1990-1992, the fertilizer input rates were obtained from Mattikalli and Richards (1996). The reports of the British Survey of Fertilizer Practice not only provided overall N consumption per hectare for each year but also provided average field rates for major tillage crops. Based on this study, the average field rates can be used to estimate N fertilizer application across GB when considered in conjunction with the CEH land cover map and June Agricultural Census (Defra (2015a)). The British Survey of Fertilizer Practice reported an uncertainty of ±9% (SEM) in the input of inorganic fertilisers.

### 2.2.4 N outputs

Atmospheric emissions considered here include: $NH_3$ volatilisation, NOx (NO, $NO_2$ and $N_2O$) and industrial emissions of $N_2$ (the $N_2$ emission from denitrification considered in denitrification pathway). The record of N gas ($NH_3$, NOx) includes those emissions from agriculture and industrial sources across GB and was obtained from UK's NAEI. The UK's NAEI provides $NH_3$, NOx (NO, $NO_2$ and $N_2O$) emission maps at a 1 $km^2$ resolution across GB, but does not include terrestrial or aquatic denitrification to $N_2$ nor emissions of $N_2$ from industrial sources. Although there are no records of industrial emissions of $N_2$ for GB, industrial $N_2$ emissions can be calculated from estimates of industrial C emissions (i.e. because hydrocarbon fuel when combusted releases both N and C). UK greenhouse gas C emissions have been recorded since 1990 (Jackson et al. 2009; Jones et al. 2017). If the C/N ratio for each carbon-based fuel is known, then the total amount of N from industrial sources

can be estimated. From previous reviews, solid fuel values have been estimated for bituminous coal (C:N = 0.011 to 0.020; Burchill and Welch 1989); petrol (C:N = 0.001 to 0.024; Rickard 2008); and natural gas (C:N= 0.000 to 0.071; Neuwirth 2008). Using these estimates, the $N_2$ released from industrial activities can be calculated as the difference between total N predicted in the combustion of fossil fuels and the recorded industrial emissions (NOx and $NH_3$). During the combustion process, only high-temperature (typically greater than 1600 °C) burning of fuels can fix atmospheric $N_2$ to NOx. But this process only has an effect on N species and does not result in additional N release or uptake from atmosphere. This study is primarily concerned with the total N budget and not the individual species as high temperature conversion of $N_2$ to NOx does not alter the mass of atmospheric N. Due to a lack of information concerning the distribution of industrial $N_2$, here industrial $N_2$ is assumed directly proportional to population. Population increase leads to increased industrial N sources, which means that industrial N sources are related to population. Due to a lack of available N emission data for each grid cell,re is no other information that can be used to distribute total industrial N emission to every grid cell, this study used population data used to spatially distribute total industrial N. Therefore, the total amount of industrial $N_2$ emissions for GB was divided by the total GB population to estimate the industrial $N_2$ emission per person. The spatial distribution of industrial $N_2$ emissions was then calculated from the spatial distribution of the GB population. The NAEI emissions data are not accompanied by uncertainty estimates, herein we use a conservative uncertainty estimate of ±80% (SEM). Uncertainty of industrial $N_2$ emission calculated from the variation in C/N

ratio of carbon-based fuels was estimated at ±50% (SEM).

In this study, denitrification includes both terrestrial denitrification and aquatic denitrification. Van Breemen et al. (2002) provided fixed rates of terrestrial denitrification for a range of land uses and estimated that denitrification rates represented 35% of N input. Different land uses have a different ability to denitrify, a spatially-differentiated total N budget should consider denitrification rate according to different land uses. Barton et al. (1999) examined 95 studies of $N_2$ flux from natural systems and calculated a value of annual $N_2$ flux based on different land uses. Here the terrestrial denitrification $N_2$ rate according to land use as estimated by Barton et al. (1999) to calculate the amount of denitrification $N_2$ distribution across GB. Unfortunately, the study of Barton et al. (1999) has not been updated. In this chapter, the land use of GB was classified as forest, grazing land, grassland and crop land. The amount of terrestrial denitrification to $N_2$ was estimated by the annual $N_2$ denitrification rate on different land uses multiplied by the areas of different land use. Throughout this study, it is assumed that the eventual product of denitrification is $N_2$, even if the eventual emission was the less reduced form $N_2O$. The soil moisture is a key limiting factor of denitrification. However, soil moisture was not explicitly used in the calculation of denitrification. Denitrification rate used in this thesis have implicitly accounted soil moisture because they rely on mass balance from real observations. The uncertainty of denitrification was assumed to be ±96% basis on SEM by Barton et al. (1999).

The concentration of different N species and river discharge have been recorded at the tidal limit as part of the UK's Harmonised Monitoring Scheme (HMS; Bellamy

and Wilkinson 2001). River discharge data and concentration data from HMS can be used to calculate the flux of different N species at the tidal limit. If N losses which occur between terrestrial source and the end of the fluvial network (in-stream loss) are known, the N loss at the terrestrial source can be estimated by subtracting the in-stream loss from the N flux at the tidal limit. Using the method of Rodda and Jones (1983), Worrall et al. (2012a) calculated the flux of different N species for each catchment (all rivers with annual discharge greater than 2 $m^3 s^{-1}$ in UK). Using this data, the relationships between different N species fluxes and catchment characteristics (including soil type and land use) were established through multiple linear regression analysis. Identification of a significant relationship between N flux and catchment areas can be indicative of in-stream loss. The regression model can be used to estimate the fluvial N loss by evaluating catchment characteristic. Worrall et al. (2012a) classified dominant soil into mineral soil, organic-mineral soil and organic soil based on the classification system of Hodgson (1997). The present study uses the method of Worrall et al. (2012a) to map GB at a scale of 1$km^2$ based on soil type and land use. The statistical model used was:

$$\begin{aligned} TDN_{flux} = 5.6\,Urban + 4.3\,Grass + 1.4\,Arable + 4.9\,Mineral \\ + 6.4\,OrgMin + 5.9\,Organic - 0.8\,Ksheep - 5.4\,Area \end{aligned} \tag{2.2}$$

where *TDN* (total dissolved nitrogen) flux is total annual average N flux (tonnes N $yr^{-1}$), *Urban* is the area of urban area in the catchment ($km^2$), *Grass* is the area of grass land in the catchment ($km^2$), *Arable* is the area of arable land in the catchment ($km^2$), *Mineral* is the area of mineral soils in the catchment ($km^2$), *OrgMin* is the area of organic-mineral soils in the catchment ($km^2$), *Organic* is the area of organic soils in the catchment ($km^2$), *Ksheep* is the number of 1000 head of sheep, the sheep

number per hectare was calculated based on a ratio of 3.1 sheep per cow (Johnes and Heathwaite, 1997), and *Area* is the area of the catchment ($km^2$). Eq. (2.2) was used to calculate the flux of different dissolved N species at the tidal limit and soil source.

Worrall et al. (2014) constructed a statistical model of fluvial flux of particulate organic nitrogen (PON) using a similar method as described above. The statistical model used to calculate PON was:

$$PON_{flux} = 213 + 0.4Grass + 0.4OrgMin + 0.5Organic - 0.13Area. \quad (2.3)$$

The variable terms are as defined above. Eq. (2.2) and Eq. (2.3) can be interpreted as an export coefficient model that was used to predict N fluvial losses at the source for each 1 $km^2$ grid based on current land use and soil type maps. The standard error on each coefficient from published sources and the uncertainty of fluvial flux based on different land use and soil types varied between ±28% and ±45% depending on the N species in the flux and the mixture of land use and soil types within any particular 1 $km^2$ grid square.

Although the net in-stream loss can be calculated from comparison of N flux from catchments of difference size (as catchment size becomes a proxy for in-stream residence time) by Eq. (2.2) will have included the N flux into groundwater, or indeed from groundwater to the stream network, a portion of N flux will be from the terrestrial biosphere via direct recharge to groundwater instead of entering the river network. Herein direct recharge to groundwater was considered as a net N output pathway (loss to groundwater) because since 1990 nitrate concentrations have increased in UK groundwater (Stuart et al. 2007), and so the flux to groundwater was

considered as a net N output even though some proportion of N in groundwater will contribute to the N fluvial flux. Stuart et al. (2007) calculated that the nitrate sink to UK groundwater occurs at a rate of 15 $\times 10^3$ tonnes N/yr which was considered here as total amount of N loss to groundwater. To obtain groundwater N loss at a scale of 1 km$^2$, the total amount of groundwater loss was evenly distributed at a 1 km$^2$ scale across all areas delimited in the aquifer map of GB (British Geological Survey, 2017). Stuart et al. (2007) reported an uncertainty estimate for groundwater N loss of $\pm$50% basis on SEM and this uncertainty was adopted here.

The N flux from human sewage and industrial waste direct to the surrounding shelf sea were reported by the Oslo and Paris commission (Commission OSPAR 2015). The direct N flux from tidal gauged areas has already been accounted for in the output pathway of fluvial N flux at soil source. Although the human sewage and industrial waste does not come from the soil, the direct N flux from ungauged areas beyond the tidal limit were accounted for in this pathway (N direct loss). From the Commission OSPAR (2015) report, values are reported for the upper and lower limit of direct loss of nitrate from GB to the surrounding shelf seas. The value of upper and lower limit are assumed as range for the N flux direct loss to the surrounding shelf sea. Because the resolution of model described here was 1 km$^2$, the total areas beyond the tidal limit were assumed to be the sum of the ungauged 1 km$^2$ area adjacent to the GB coast line. Thus, direct loss per km$^2$ was calculated as the total amount of direct loss divided by total areas beyond the tidal limit. The uncertainty on this flux was reported by OSPAR as $\pm$15% basis on SEM and this uncertainty was adopted here.

Sewage produced in GB is treated within sewage treatment plants. Treatment of wastewater can lead to formation of $N_2O$ (Parravicini et al. 2016). In this study, sewage was assumed to be generated by humans. Because the average healthy adult does not accumulate N in their body, N consumed in the average healthy adult diet was used as an estimate of human sewage output. The difference between human sewage output and fluvial loss (sewage sludge return to land have accounted in this pathway) in urban areas (as predicted by Eq. (2.2) and Eq. (2.3)) was used to estimate the gas emission from sewage treatment plants. The total gas emission from sewage treatment plants can be spatially distributed across urban areas using population estimates. Sewage processed in treatment works comes from the areas where people live. If N exports from treatment works were not distributed by population, the result could not present the spatial distribution the source of N sewage output. No uncertainty estimates were available for this flux pathway, thus ±80% on basis SEM was used as the default uncertainty.

### 2.2.5 Uncertainty analyses in N budget

The uncertainty of the total N budget was considered for each 1 $km^2$ grid of GB using the individual uncertainties estimated for each pathway as detailed above. This study assumed that the uncertainty of the input and output data can be characterized by their statistical distribution functions. Monte Carlo simulations were used to quantify the overall uncertainty for all pathways for each 1 $km^2$ grid. A total of 1000 Monte Carlo simulations were performed using Matlab as initial experimentation showed that any more than 1000 Monte Carlo simulations still produced a

similar result. This number (1000) was chosen because the model generally converged at this point.

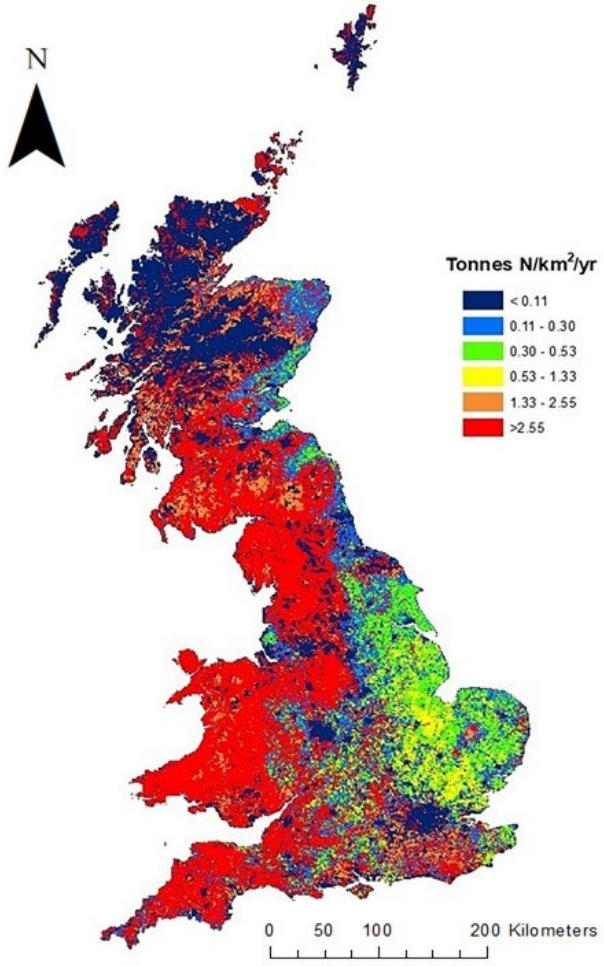


**Figure 2.2:** Assumed Rate of Biological Nitrogen Fixation for 2015.

## 2.3 Results

### 2.3.1 Inputs of total N

The N fixation rates were determined to be: 4 tonnes N/km$^2$/yr for bean and pea crops; 15 tonnes N/km$^2$/yr for clover; 0.04 tonnes N/km$^2$/yr for temperate forest; and 4.70 tonnes N/km$^2$/yr for grass. The distribution of BNF across GB (Figure 2.2)

depends largely on land use (areas with high fixation rate crop present high BNF flux), thus, higher values are observed in the northwestern England and Wales and the lowest values are observed in northern and western Scotland.

The total N deposition data were not vegetation-specific but were based on a grid-average of multiple land classes. Total N deposited to land ranged from 0.3 to 4.5 tonnes N/km$^2$/yr and averaged 1.3 tonnes N/km$^2$/yr. The high N deposition rates were assumed to occur in urban areas and areas with intensive agriculture (Figure 2.3). The high rates of N deposition found in the areas of the Scottish-English border, the Pennines and Welsh mountains can be ascribed to high annual precipitation in these regions. In addition, some areas close to intensive agriculture, such as East Anglia, also exhibit high N deposition rates. In contrast, low N deposition rates (below 0.76 tonnes N/km$^2$/yr) are observed in north-west Scotland where there are few local industrial or intensive agricultural emission sources or urban areas.

The food and feed transfer pathway was divided into a livestock N balance, a human N balance, and a crop N balance. As stated previously, the human N balance is equivalent to human N intake minus human N output. N intake (i.e. human N dietary consumption) was previously determined by the FAO to be 4.56 $\times 10^{-3}$ tonnes dry matter/yr (World Health Organization 1974). Because the human N output pathway has already been accounted for in the sewage flux loss, if N output by human included again in the calculation of human N balance, the human N output may get doubled counted. Human N balance can be calculated here by human N consumption alone. Therefore, the GB spatial distribution of human N balance is equivalent to the distribution of the GB population (Figure 2.4). The livestock N

balance was determined to be an output from GB with values varying from 0.5 $\times 10^{-3}$ tonnes N/head to 10.5 $\times 10^{-3}$ tonnes N/head (Table 2.1). Maximum input from food and feed transfer were observed in grassland areas where livestock populations are the highest (Figure 2.5). Conversely, the livestock export was assumed to be zero in urban areas.

**Table 2.1:** Livestock N export per head.

| Item | Output | | Number | N export for each category |
|---|---|---|---|---|
| | (Total N tonnes) | | (head) | ($\times 10^{-3}$ tonnes N/head) |
| Sheep | Meat | 22,100 | 43,304,000 | 0.65 |
| | Wool | 6,800 | | |
| Cattle | Meat | 48,100 | 11,856,000 | 10.50 |
| | Milk | 75200 | | |
| Pig | Meat | 35,500 | 7,627,000 | 4.65 |
| Poultry | Meat | 58,500 | 142,266,000 | 0.50 |
| | Egg | 12,500 | | |

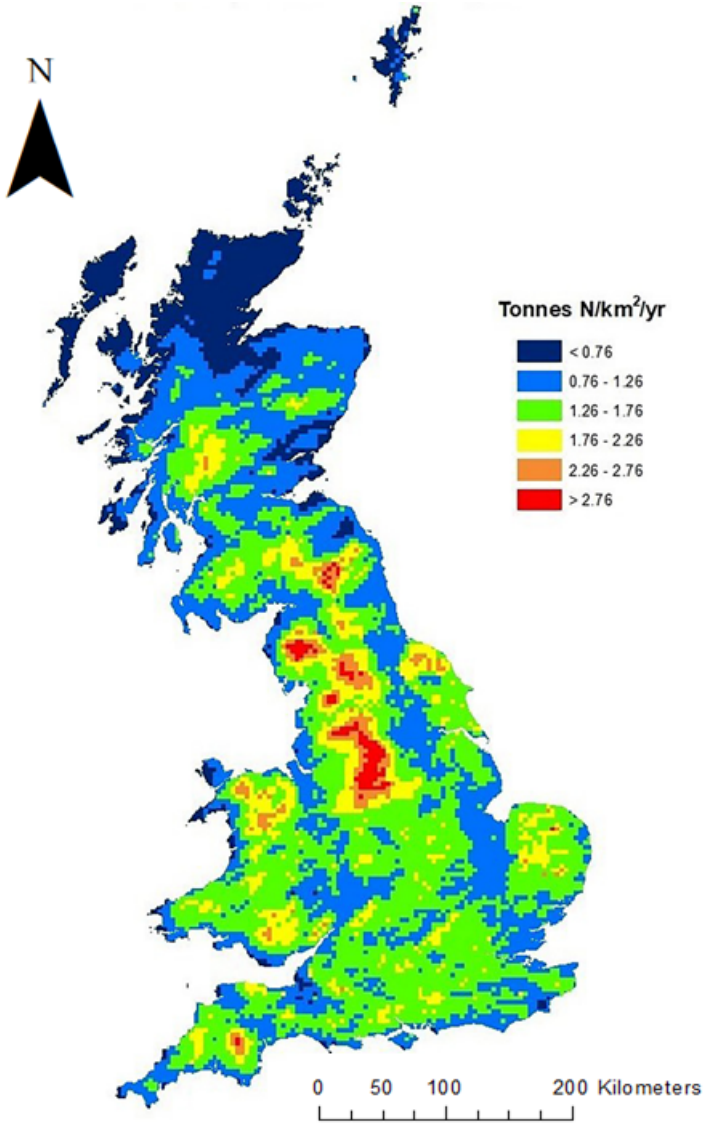


**Figure 2.3:** Assumed Rate of Total Nitrogen Deposition for 2015.

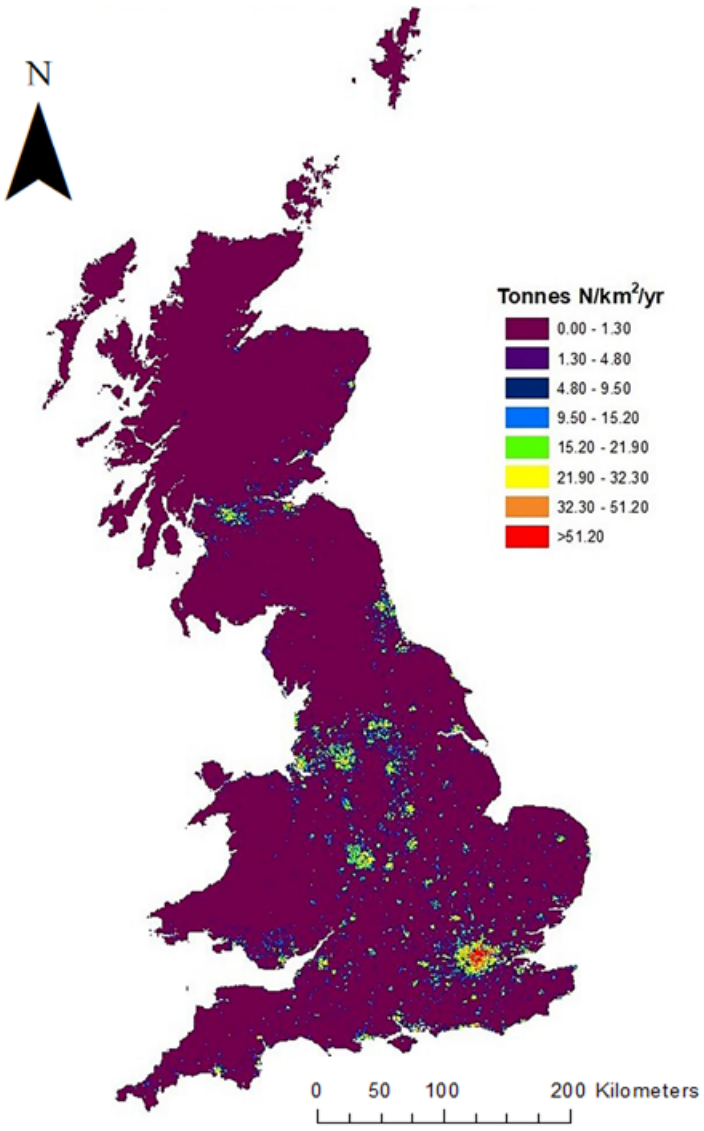


**Figure 2.4:** Assumed Rate of Net Nitrogen Consumption by Human for 2015.

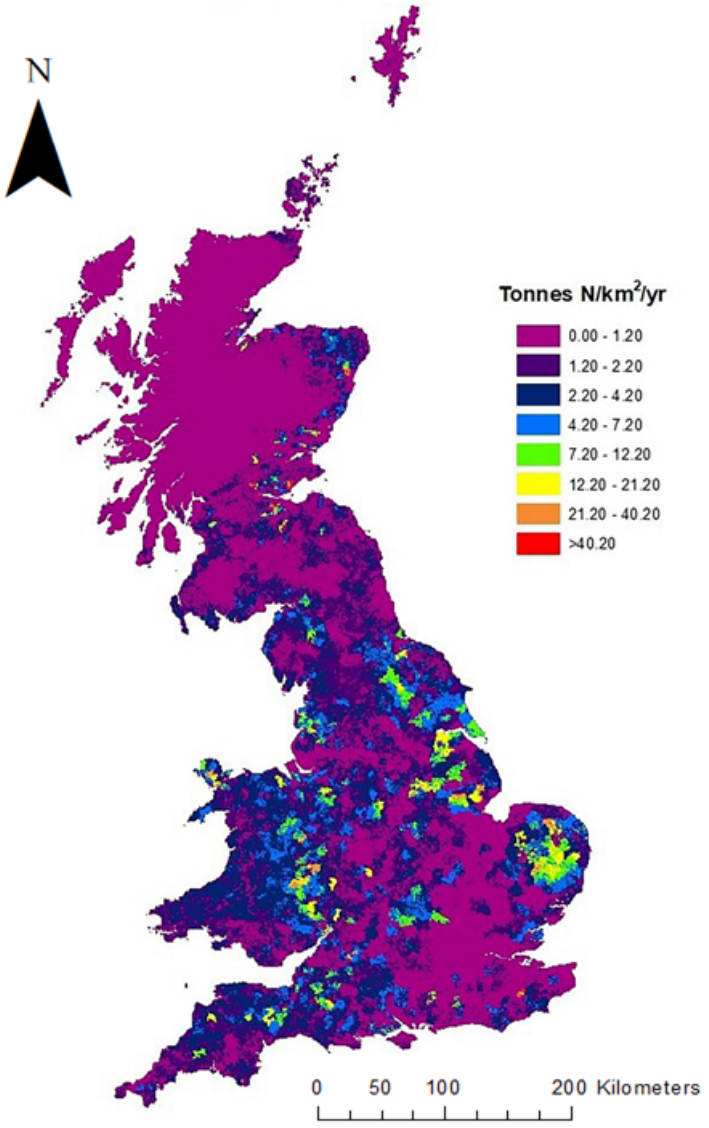


**Figure 2.5:** Calculated Rate of Net Nitrogen Consumption by livestock for 2015.

Total N input of inorganic fertilizer was the largest N input into GB. The average fertilizer rate on different cropping varied from 3.0 tonnes/km$^2$ for peas to 21.1 tonnes/km$^2$ for oilseed rape. The average value of all crops and grass was 13.8 tonnes/km$^2$. The largest fertilizer input was in eastern England where land use is predominantly agricultural arable, conversely the values decrease to zero in the Highlands of Scotland (located in the north of GB) where the land use is comprised

predominantly of mountain, heath and bog (Figure 2.6).

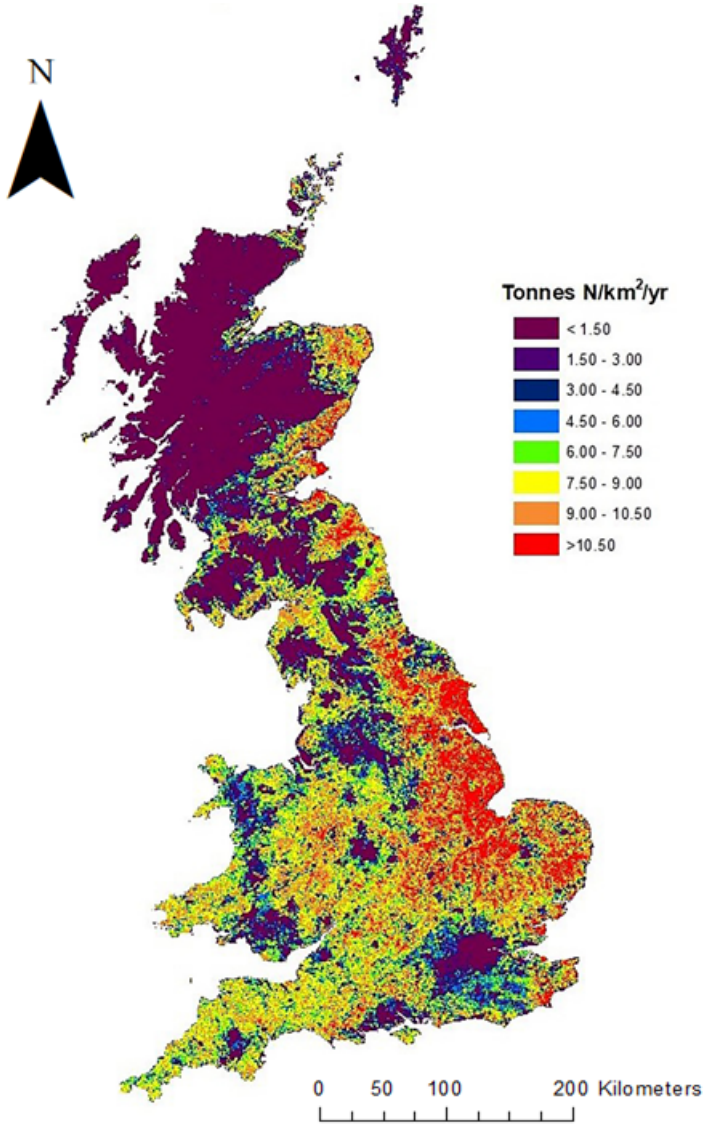


**Figure 2.6:** Calculated Rate of Inorganic Fertilizer Input for 2015.

### 2.3.2 Outputs of total N

Atmospheric N emissions account for the largest proportion of all N outputs. Combining the different types of Nr species and determining the spatial distribution of Nr revealed the highest N emission rates in agricultural areas (Figure 2.7). Conversely,

lowest N emissions were predicted in the semi-natural areas of western Scotland. The predicted spatial distribution of N emissions across GB is in agreement with previous studies. Sozanska et al. (2002) constructed a GB model for $N_2O$ flux based on different land uses and predicted the high fluxes of $N_2O$ from grassland and arable land. Davidson and Kingerlee (1997) reported NO emissions from soil with the largest emissions associated with cultivated agriculture. In addition, ammonia emission is dominated by livestock and N fertilizer application occurring in agricultural arable areas (Davidson and Kingerlee 1997). Therefore, the highest emissions of Nr species were associated with agricultural arable (Figure 2.7). Within agricultural arable, N species emissions were controlled by N applied and deposited in this land use, such as fertilizer and atmospheric deposition.

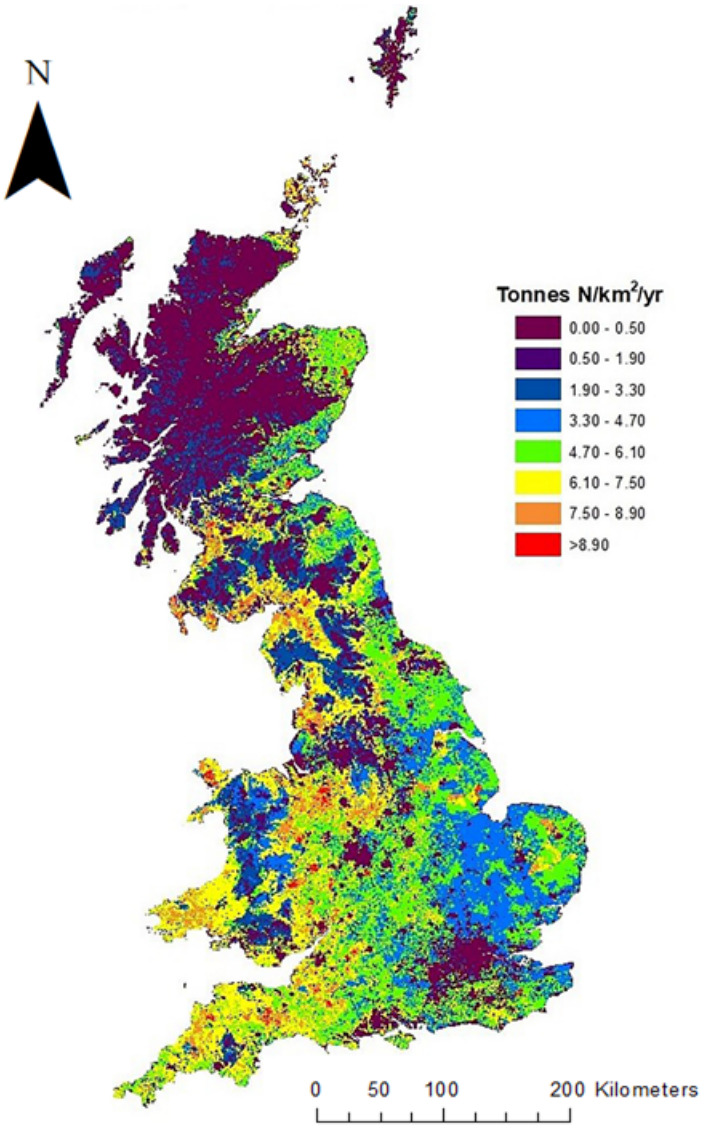


**Figure 2.7:** Calculated Atmospheric Nitrogen Emission for 2015.

The total industrial $N_2$ emission rates for GB, according to NAEI estimates, were 262 $\times 10^3$ tonnes N/yr $\pm$80% on basis SEM. Total amounts of industrial $N_2$ emission were distributed by population and so giving an average emission of 0.004 tonnes N/ca/yr. Industrial $N_2$ emission rates were distributed by population, therefore, the distribution of industrial $N_2$ was the same as the distribution of population where urban areas (such as London, Liverpool and Leeds ) having a higher industrial $N_2$

emission output (Figure 2.8).

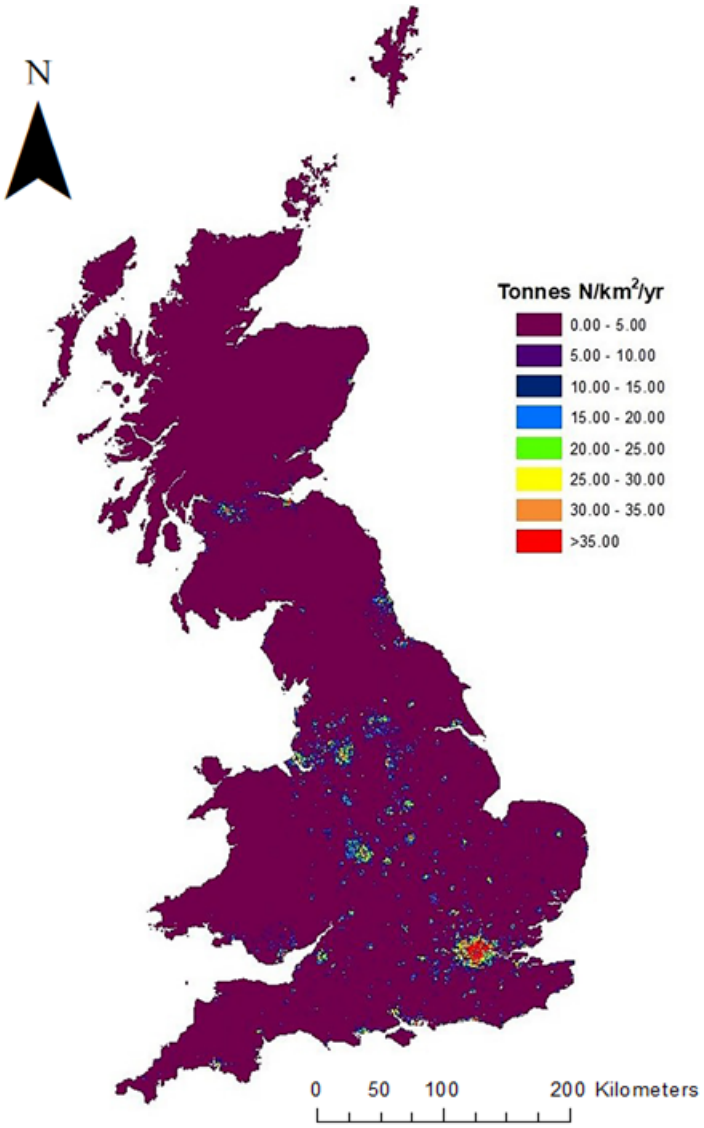


**Figure 2.8:** Assumed Rate of Industrial $N_2$ Emission for 2015.

Terrestrial denitrification to $N_2$ according to different land uses from Barton et al. (1999) varied from 0.00 tonnes N/km$^2$/yr to 1.34 tonnes N/km$^2$/yr (Table 2.2). The available land use data only distinguished grassland rather than discriminating between improved and unimproved grassland – the latter having no fertilizer applied to it. As can be seen from Table 2.2, the value for terrestrial denitrification to $N_2$ from grass land was 0.93 tonnes N/km$^2$/yr calculated from the weighted mean of

fertilized grass land and rough grazing land based on Barton et al. (1999). The predicted denitrification map reveals the spatial distribution of terrestrial denitrification to $N_2$ according to different land use across GB (Figure 2.9). Terrestrial denitrification to $N_2$ rates are predicted to be highest in eastern England, associated with arable land use and lower in western England which has more grass land areas.

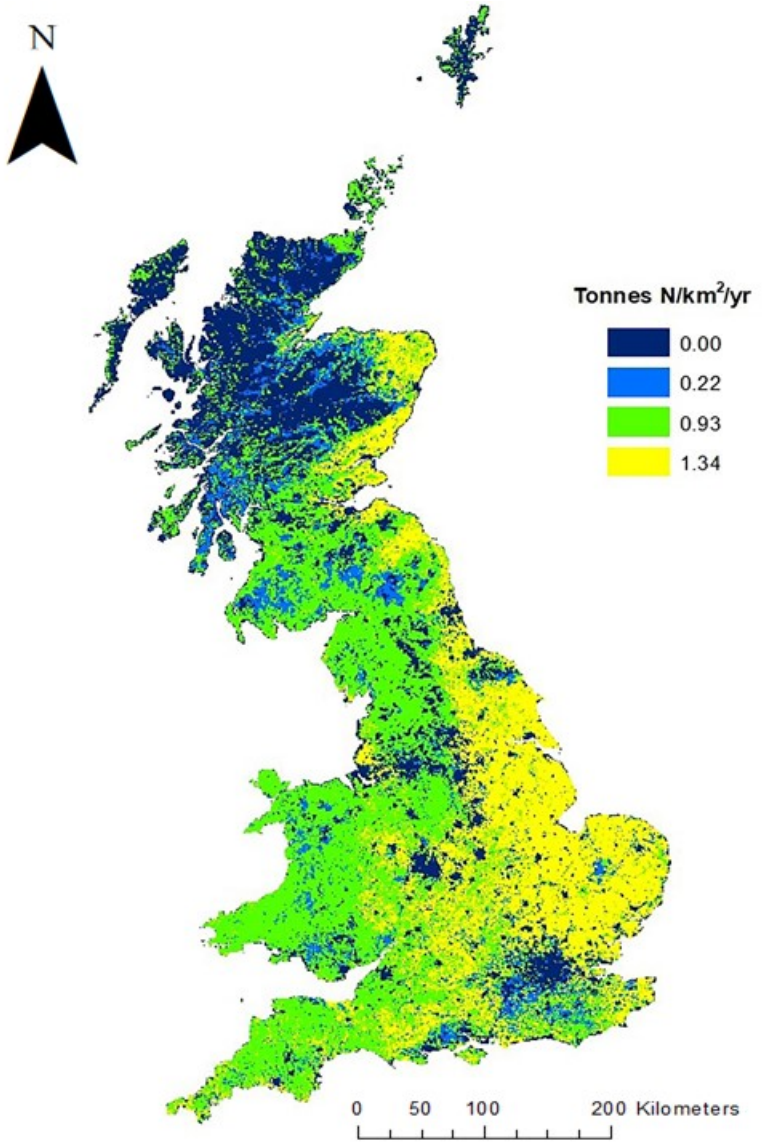


**Figure 2.9:** Assumed Rate of Denitrification to $N_2$ for 2015.

**Table 2.2:** Denitrification rate assumed for different land uses. *Source: From Barton et al. (1999)*

| Land use | | Preferred value (tonnes N/km$^2$/yr) |
|---|---|---|
| Forestry | | 0.22 |
| Grassland | Fertilizer grassland 1.34 | 0.93 |
| | Rough grazing land 0.32 | |
| Crop | | 1.34 |
| Other land use | | 0 |

Total N fluvial flux at 1 km$^2$ according to different land use varies from 0.00 tonnes N/km$^2$ to 12.40 tonnes N/km$^2$ and the spatial distribution of N fluvial flux can be seen in Figure 2.10. The estimated uncertainty on the N fluvial flux calculation is summarized in Table 2.3. Northwestern England and western Wales reveal the largest fluvial export of total N.The BNF and fertilizer input as important N input should be higher in here, but most areas of northern and western Scotland have a lower BNF rate ranging from 0.00 to 0.30 tonnes N/km$^2$/yr. The fertilizer input was also quite low areas of northern and western Scotland, ranging from 0.00 to 3.00 tonnes N/km$^2$/yr. Although these N input pathways are lower in the highlands of Scotland than in eastern England (fertilizer input 4.51~13.73 tonnes N/km$^2$/yr, BNF 2.21~4.70 tonnes N/km$^2$/yr), the Scottish Highlands are still predicted to export 4.50 to 6.50 tonnes N/km$^2$ and much of this could be as DON rather than as inorganic N.

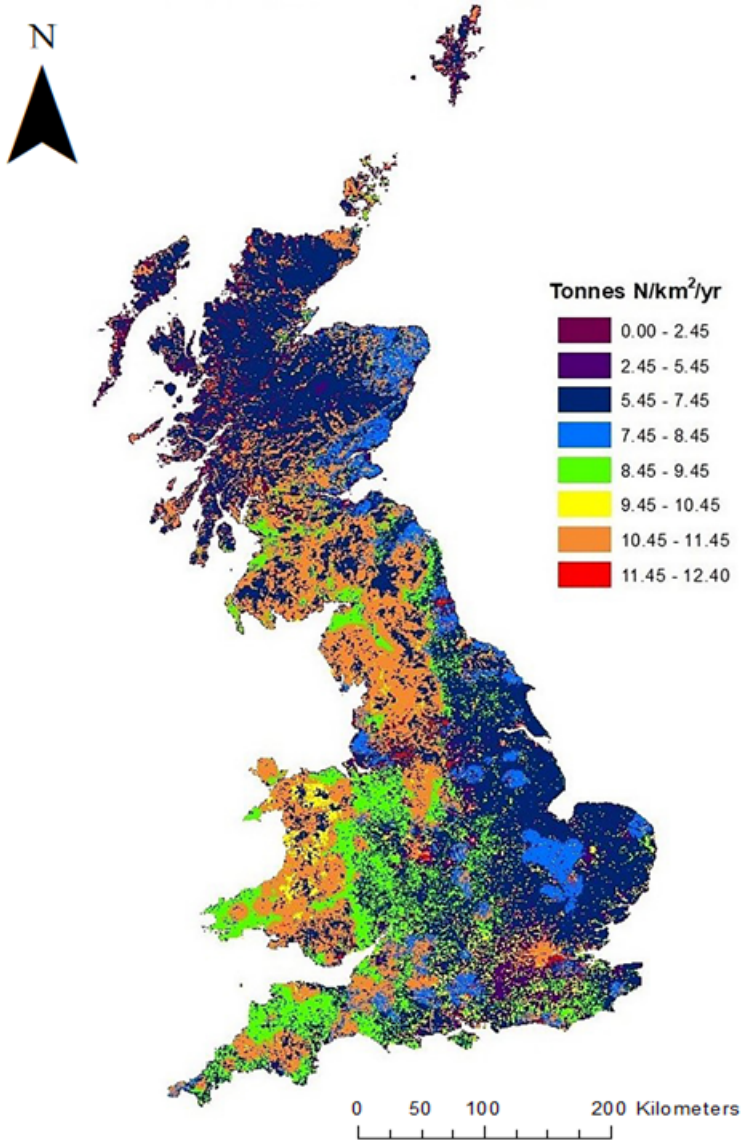


**Figure 2.10:** Predicted Fluvial Loss of Total Nitrogen for 2015.

The groundwater loss (N direct recharge to groundwater) per year in aquifer areas was previously reported by Stuart et al. (2007) as 15 $\times 10^3$ tonnes N /yr since 1990. The average value of ground water loss in aquifer areas was 0.07 tonnes N/km$^2$/yr calculated from total ground water loss and aquifer areas. The distribution map of groundwater loss (Figure 2.11) follows the map of UK aquifers.

**Table 2.3:** Summary of the source of information for every N pathway and uncertainty.

| Input | Data source | Uncertainty |
|---|---|---|
| Biological nitrogen fixation | Smil (1999); Cleveland et al.(1999) MAFF(1987-2000); CEH | ±25% |
| Atmospheric deposition | CEH: www.ceh.ac.uk | ±80% |
| Inorganic fertilizer | British Survey of Fertilizer Practice | ±9% |
| Human consumption | | ±80% |
| Livestock consumption | | ±80% |
| Output | | |
| Atmospheric emission of $N_2O$, $NH_3$ | Naei.defra.gov.uk | ±80% |
| Atmospheric emission of $N_2$ | NAEI, Burchill and Welch (1989), Rickard and Fulker (1997), Neuwirth,2008. | ±50% |
| Terrestrial denitrification to $N_2$ | Barton et al. (1999), MAFF (1987-2000), Defra(2001-2013), Forestry Commission(2015) | ±96% |
| Groundwater | Stuart et al. (2007) | ±50% |
| Direct waste losses | OSPAR Commission | ±15% |
| Fluvial N losses | Harmonised monitoring scheme; Worrall et al.,2014; Neal and Davies,2003; | ±28% to ±45% |

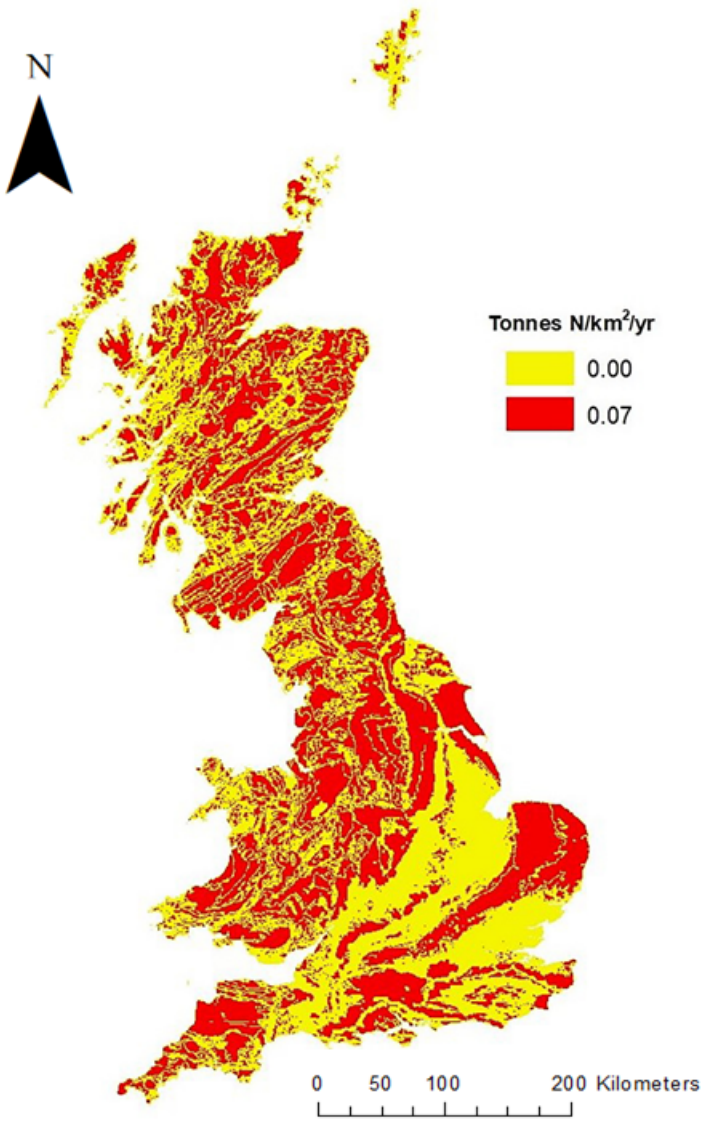


**Figure 2.11:** Assumed Nitrogen Loss Calculated from Groundwater for 2015.

The total amount of direct N loss beyond tidal limit export to marine areas was estimated to be 58 ($\pm 9$) $\times 10^3$ tonnes N in 2015 (Commission OSPAR 2015). The direct N loss beyond tidal limit was distributed in the ungauged 1 km$^2$ area adjacent to the GB coast line. The value of direct N loss of 6.8 tonnes N/km$^2$/yr was calculated from total N direct export to marine areas and total ungauged areas, the distribution of direct N loss is shown in Figure 2.12.

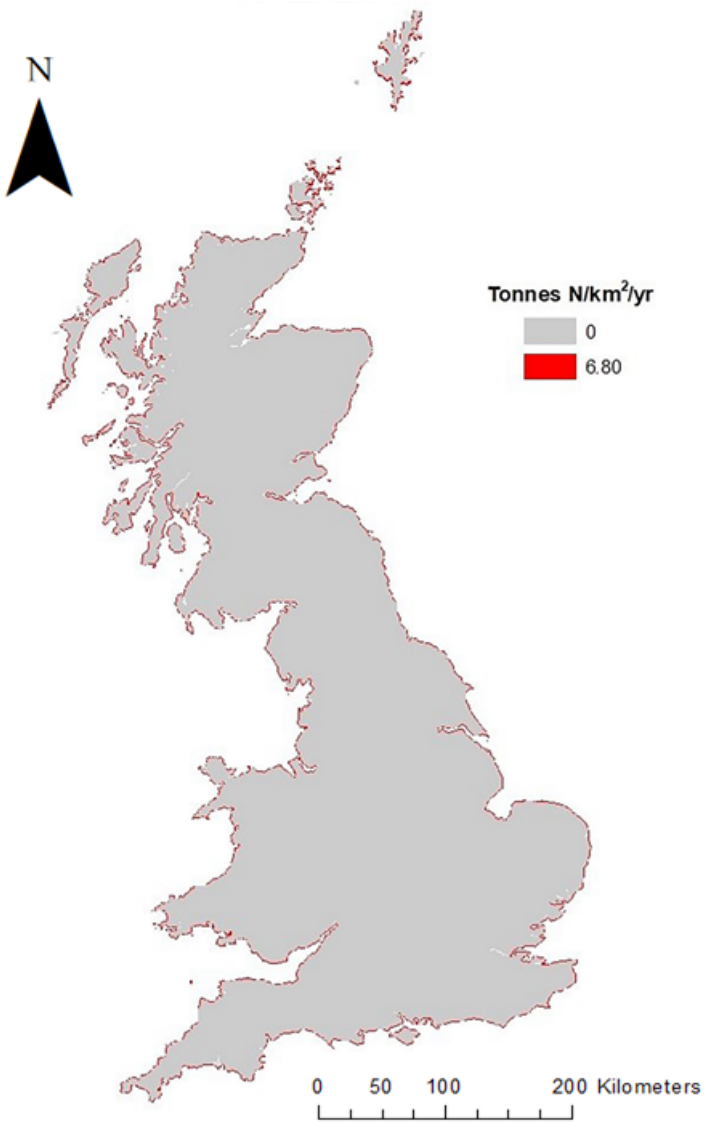


**Figure 2.12:** Assumed Direct Nitrogen Loss Beyond Tidal Limit for 2015.

The N gas emission rates from sewage treatment plants by population was determined to be 0.0019 tonnes N/ca/year. Because all major sewage treatment plants are located in or near urban areas, CEH land use maps were used to identify urban (rural) areas for inclusion in (exclusion from) the calculation (Figure 2.13).

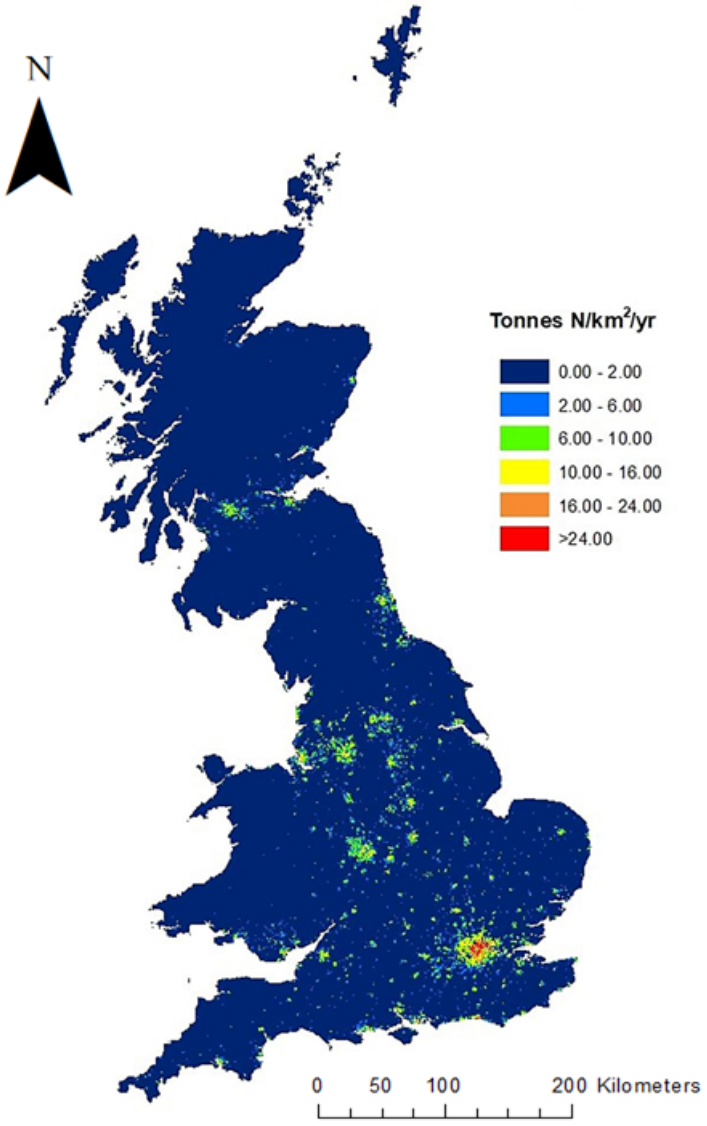


**Figure 2.13:** Calculated N Gas Emission From Sewage Treatment Plant for 2015.

The calculated net N output from the terrestrial biosphere was obtained from N surplus of crop. In this chapter, the grass N removal rate was negligible as it has already been considered as an internal transfer with livestock (the grass to livestock return to the land by waste). The average value of arable crop N removal was determined to be 9.48 tonnes N/km$^2$ with a value of 0.00 tonnes N/km$^2$ for non-arable land use. The spatial distribution of crop offtake follows that of arable land

across GB (Figure 2.14).

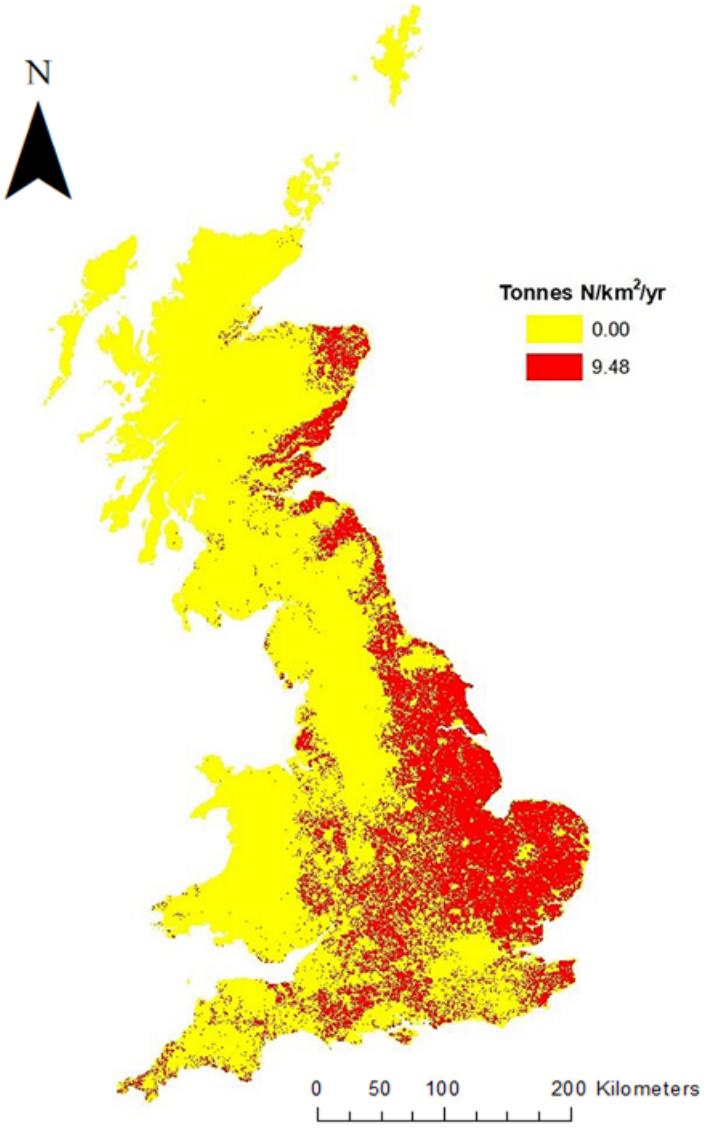


**Figure 2.14:** Calculated Nitrogen Loss from Crop Offtake for 2015.

The overall total N budget can be calculated by combining all major N inputs and outputs across GB based on 1 km$^2$ resolution. Table 2.4 details the total N budget of GB based upon the calculated values for each of N the input and output pathways. Inorganic fertilizer was the largest N input into GB which accounted for 60% of total N input. A spatially-differentiated total N budget of GB was

constructed by calculating the difference between all inputs of N and all outputs of N (Figure 2.15). The 95% confidence interval of total N budget is shown in Figure 2.16 and Figure 2.17. Moreover, Figure 2.18 which represent the distribution of sinks and sources that are 95% confident less or greater than zero. For the whole of GB, 66% of 1 km$^2$ grid squares are net N sources while 34% of the 1 km$^2$ grid squares were estimated to be net N sinks.

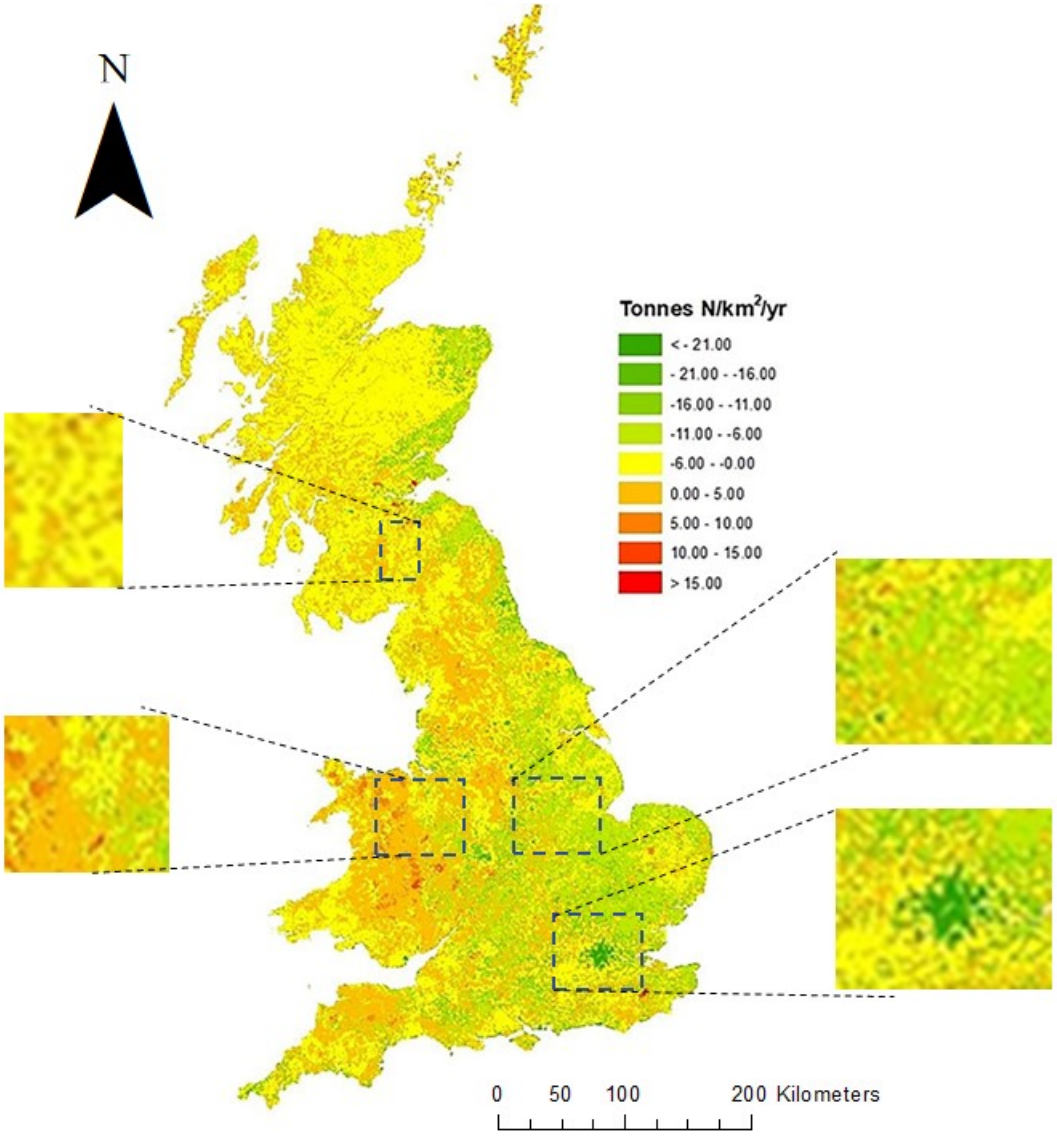


**Figure 2.15:** Calculated Total Nitrogen Budget of Great Britain at 1 km$^2$ for 2015

**Table 2.4:** Summary of calculated median values of N inputs and outputs for 2015; and proportions of N inputs or outputs in 2015.

| | Flux in 2015 $(10^3 tonnes N/yr)$ | Proportions of N inputs/outputs |
|---|---|---|
| Input | | |
| Biological N fixation | 505 | 18% |
| Atmospheric deposition | 306 | 11% |
| Food and feed import | 295 | 11% |
| Inorganic fertilizer | 1650 | 60% |
| Sub-total | 2756 | |
| Output | | |
| Atmospheric emission | 845 | 22% |
| Terrestrial denitrification | 173 | 5% |
| Fluvial loss at soil source | 1823 | 48% |
| Direct sewage flux | 58 | 2% |
| Ground water loss | 15 | 0.4% |
| Gas emission from sewage treatment plants | 47 | 1% |
| Industrial emission | 261 | 7% |
| Crop remove | 579 | 15% |
| Sub-total | 3801 | |
| Total N budget | 1045 | |

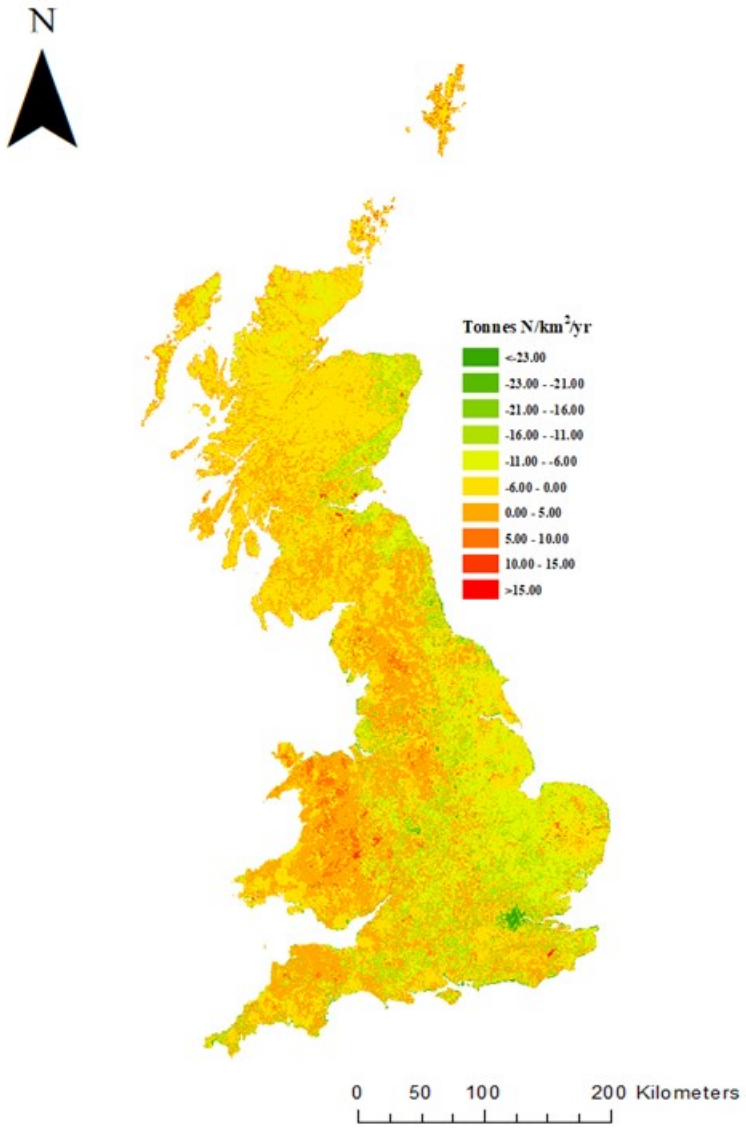


**Figure 2.16:** The lower limit of the asymptotic 95% confidence interval for N budget of 2015.

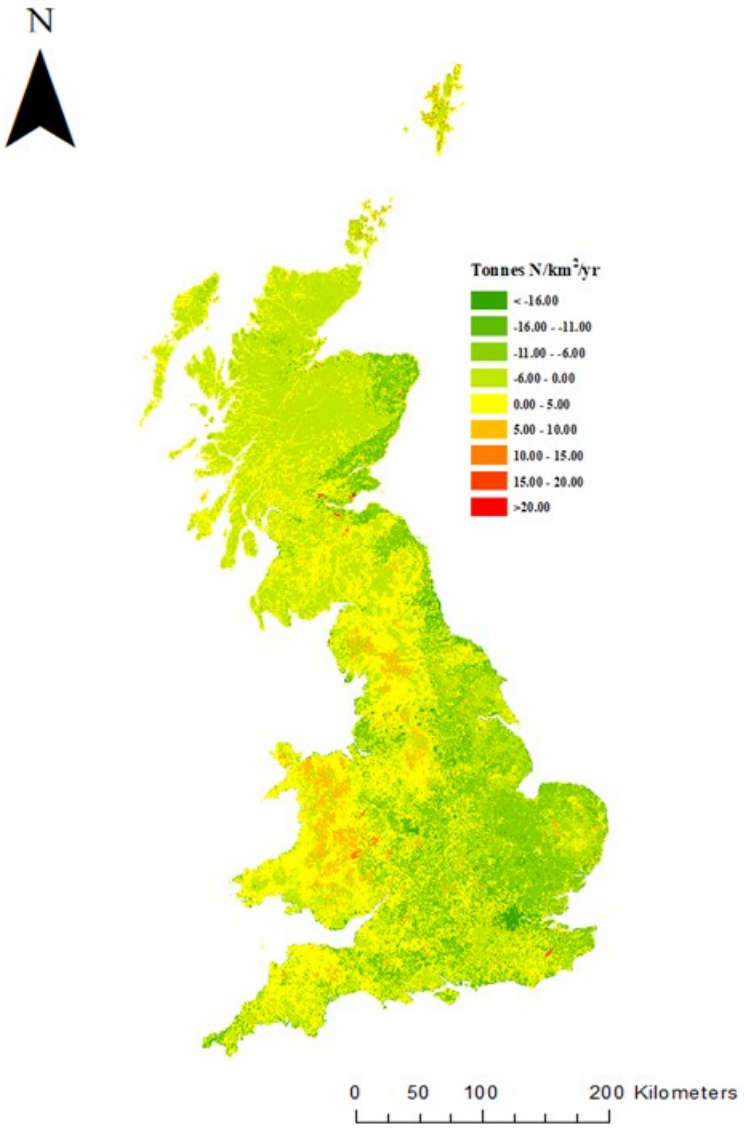


**Figure 2.17:** The upper limit of the asymptotic 95% confidence interval for N budget of 2015.

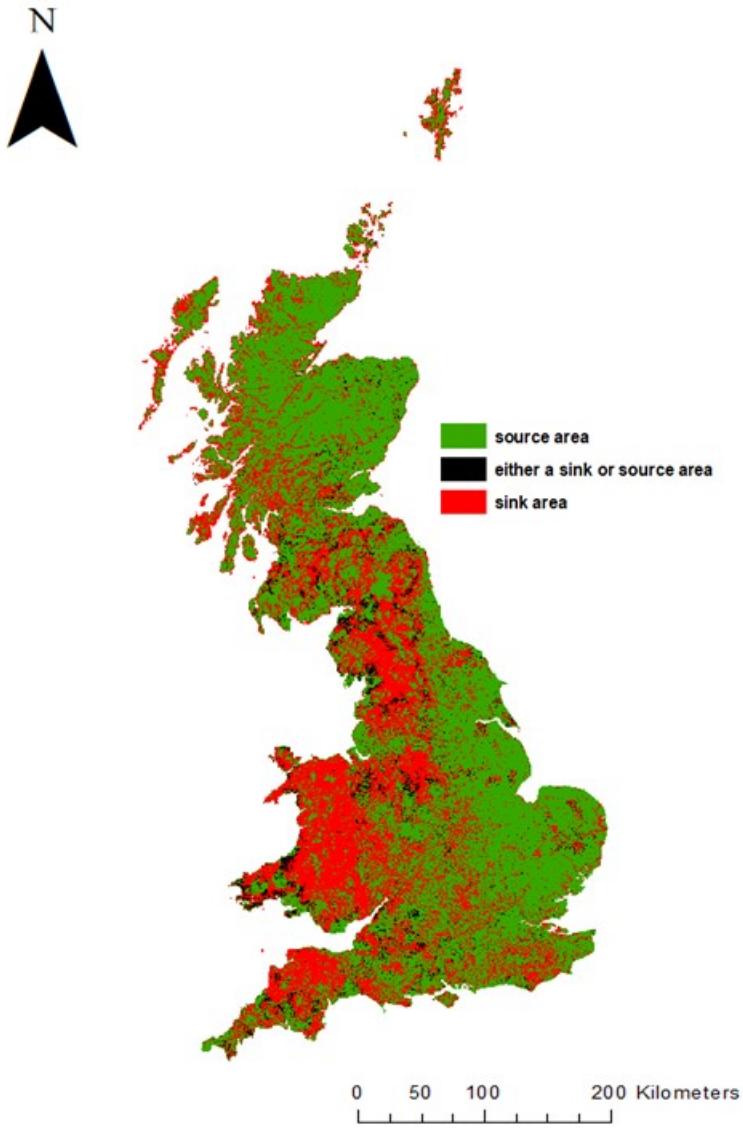


**Figure 2.18:** The distribution of sink and source areas at a 95% probability for N budget of 2015.

## 2.4 Discussion

This chapter is the first attempt to construct a spatial total N budget for a country including all possible N inputs and outputs. On this map, positive values represent sinks in which inputs to the soil exceed losses from the soil. Conversely, nega-

tive values represent sources where losses from the soil exceed inputs to the soil (Figure 2.15). For each individual 1 $km^2$, there is considerable spatial variability in total N inputs, ranging from 0.68±0.21 tonnes N/$km^2$/yr in northern Scotland to 73.86±22.16 tonnes N/$km^2$/yr in London. The largest N output areas are also found in London where the mean value was -112.71 tonnes N/$km^2$/yr. The lowest value of total N output areas was -0.71 tonnes N/$km^2$/yr, found in the northwestern Scotland. At a national scale, the total N budget for 1 $km^2$ grids ranged from -21±3 tonnes N/yr to +34±5 tonnes N/yr. Major sink areas were located in western England and north Wales where fertilizer N application and BNF rates are high and dominate the N input. Furthermore, high fertilizer application also leads to high local predicted N deposition in those areas. The major N source areas are located in big cities (e.g. London, Manchester, Birmingham, Leeds, Liverpool and Edinburgh). The total N output are highly correlated with population density, indicating the high population enhances N output. In addition, predicted NO and $NO_2$ emissions released from those areas are higher than other areas due to fossil fuel combustion (e.g. via natural gas combustion in domestic central-heating boilers and power stations).

In this chapter, 66% of GB was determined to be a source area with 34% identified as a sink area in 2015. In GB, population increased from 54.38 million in 1971 to 64.17 million, an increase of 0.4% per year and GB population will continue to grow in the future (Office for National Statistics). In this chapter, industrial $N_2$ emissions, N gas emissions from sewage treatment plants and food input were assumed to have a direct relationship with population size whereas other pathways

were not. To account for population influencing N fluxes, a correlation analysis between population and the total N budget for all 1 $km^2$ grid squares was conducted. A significant positive correlation between total N budget and population was found ($r^2 = 0.83$, $p = 0.033$) – as would be expected given the assumptions of this chapter. The implication is that increasing population may increase the magnitude of the total N budget. Furthermore, the total amount of N released to the environment by human activity in 2015 was -16.65 $\times 10^{-3}$ tonnes N/ca, implying that high population density areas were more likely to be source areas.

Every land use type involved sink and source areas. But the proportion of sink or source areas with each land use was not the same. The proportion of sink or source represented by each land use is shown in Table 2.5. In urban land use areas, the mean value of the N budget was -19 ($\pm 2$) tonnes /$km^2$/yr, ranging from -20.5 tonnes /$km^2$/yr to 1.2 tonnes /$km^2$/yr, 97% of urban land use areas were source areas. In grassland areas, the total N budget ranged from -2.4 tonnes/$km^2$/yr to 15.5 tonnes/$km^2$/yr with a mean value of 5.5 tonnes/$km^2$/yr. In total, 65% of grass land areas were sinks. For arable land, the mean value of the N budget was -11.8 tonnes/$km^2$/yr with only 1.5% of arable land use identified as a sink; thus, arable land use in GB can be considered as a source area. On average, arable areas lose N to the surrounding environment whereas grassland areas store organic N in the soil. This distribution of sinks and sources by land use type is consistent with Lord et al. (2002) who concluded that the conversion of grass to arable would increase N losses; furthermore, land use change alone was considered a major factor that affected the N budget. For urban land use, there is negligible inorganic fertilizer input or BNF. For

other land use (grass and arable land use), the inorganic fertilizer was the largest N input, sequentially, followed by BNF. When grass land is converted to urban land use, the total N input will become less than the total N output, thus, these areas will become N source areas. Whitmore et al. (1992a) demonstrated that the start of ploughing grass may increase the nitrate leaching. When arable land use is converted to grass land use, ploughing to plant grass seed would initially result in net mineralisation but thereafter the grass land would gradually become an N sink area.

**Table 2.5:** The proportion of sink or source under different land uses.

| Land use | Sink | Source |
|---|---|---|
| Urban land use | 3% | 97% |
| Grass land use | 35% | 65% |
| Arable land use | 1.5% | 98.5% |
| Total GB | 34% | 66% |

In this chapter, all major N pathways have been considered. However, there is no absolute test as to whether our total N budget is complete or not. One potential limitation of the present study is that the transfer of N from one year to the next is not considered. Similarly, the possibility that lags can extend over several years and in effect act as a legacy reserve of N has not been considered. Van Meter et al. (2016) showed that reducing N loads through the Mississippi basin would take decades longer than expected as legacy N stores would sustain fluxes.

Given the results it is necessary to consider where the accumulation is occurring,

and similarly, from where the loss is occurring (i.e. which reservoirs of N are being added to or denuded)? Land use change could result in considerable accumulation or denudation of soil N reserves. Table 2.5 shows that grassland is more likely to be a sink of total N than either urban areas or arable land. Therefore, conversion of grassland could result in the development of sources of N. Ploughing up of grassland will lose N in the form of mineral N (promoted soil organic N mineralization) and the N release would follow the same trend as loss of carbon from soils (Bell et al. 2011; Barraclough et al. 2015). Alternatively, part of N released from top soil will feed into the subsoil which has not been disturbed and so could represent a site of accumulation. Therefore, the accumulation of N in the subsoil represents an unexplored sink and potential "time bomb" of N in the vadose zone (Ascott et al. 2017). This study has not considered any processing within the groundwater sink and denitrification can occur within groundwater. Hiscock et al. (2003) measured denitrification rates in UK aquifers as between 0.5 to 3 tonnes N/km$^2$/yr, however, that would be of the order of 0.07 tonnes N/km$^2$/yr. For the source areas, N may be coming from denitrification of groundwater and groundwater recharge into soil. This chapter only considered the aquatic denitrification from the river surface not direct denitrification from groundwater or nitrate recharge into soil from groundwater.

The percentage of inputs and outputs in the different pathways reported are compared with other national N budgets in Table 2.6. N fertilizer application is the dominant N input in South Korea (Bashkin et al. 2002), China (Ti et al. 2012) and GB (data derived in this paper). The BNF (included natural BNF and cultivation BNF) is the dominant N source in New Zealand (Parfitt et al. 2006). In the

northeastern U.S.A, N deposition was previously found to be the largest N input (Van Breemen et al. 2002). For N output, the percentage of riverine N export was the highest of all N output pathways in South Korea (Bashkin et al. 2002), New Zealand (Parfitt et al. 2006) and GB (data derived in this paper). Denitrification and transfer to N storage were the largest N transfers in China (Ti et al. 2012) and the northeaster U.S.A (Van Breemen et al. 2002). The comparative percentage of different N pathways can give some indication that different countries may need to pursue different environmental management approaches to reducing N pollution.

N input from rock weathering has not been included in the spatial N budget of GB. Houlton et al. (2018) have calculated the N input from rock weathering for the Earth's surface and the N denudation flux was predicted at between 11 and 18 $\times 10^6$ tonnes N/yr. According to the total N denudation flux of the Earth's surface and total surface area of the Earth, the average export from rock weathering would be between 2.1 to 3.5x10$^{-}$3 tonnes/km$^2$/yr. Therefore, the export of N input from rock weathering was relatively low when compared to other N pathways and this N flux cannot usefully be distributed to the various land uses with a 1 km$^2$ spatial resolution. This study did not therefore include the N input from rock weathering. In addition, this chapter did not include N import from wood pellets (burn heating) because no data exist on N flux distribution across GB. The Department of Energy and Climate Change (DECC) has published figures detailing UK imports and exports of wood pellets since 2008 (Department of Energy & Climate Change 2015). The available data for wood pellets shows that they have become an increasingly important fuel source in UK in the past decade. The importing of wood pellets from

outside of UK represents a new flux of N into the UK. The UK had a net import of 6447 $\times 10^3$ tonnes of wood pellets in 2015. The threshold values of N in wood pellet provided by ENplus Handbook were between 0.3% and 1% (Council 2015). The new flux of N due to the net import of wood pellets would then be between 19 $\times 10^3$ tonnes to 64 $\times 10^3$ tonnes for GB. Although there is no information that can be used to distribute this N flux to a 1 $km^2$ resolution, this N flux could be used to improve the overall N budget for GB. The overall N budget of GB in 2015 (including N flux from wood pellets) would become a net sink of 1087 $\times 10^3$ tonnes N/yr.

The sink and source areas across GB were calculated for each 1 $km^2$ area and not for the terrestrial biosphere as a whole. The major difference between a total N budget for the terrestrial biosphere and one for the whole of GB is industrial emissions of NOx, $NH_4$ and $N_2$. Because there is currently inadequate spatial information about GB industrial N emissions, this study used the population density to distribute industrial N emissions across GB. For future studies, if a total N budget at the catchment scale is required, the spatial N budget presented here should be recalculated without industrial N emissions. Some degree of uncertainty in our total N budget is introduced by considering industrial N emissions equally across urban and rural areas according to population rather than excluding rural areas as an emissions source altogether; however, 17.6 % GB's people live in rural areas and a conservative uncertainty of $\pm 80\%$ was thus applied thus, we assume the industrial N emission did not impact on the type of N budget (sink or source) for rural area.

No account has been taken here of the potential effect of fertilizer application and excessive N deposition on increasing storage of N in agricultural soils. However,

recent studies based on stable isotope $^{15}N$ field experiments (Gardner and Drinkwater 2009 and Sebilo et al. 2013) have quantified the anthropogenic N (i.e. N fertilizer and N deposition) uptake by plants, export to the hydrosphere and retention in the soils by N isotope method ($^{15}N/^{14}N$ ratios was employed in investigating the sources of pollution). The source of N pollution in hydrosphere and soils mainly from the fertilizer application and excessive N deposition. Sebilo et al. (2013) found that 12%-15% of fertilizer-derived N was residing in the soil and was predicted to remain in the soil more than a quarter century after fertilizer application. Gardner and Drinkwater (2009) analysed 217 field studies which suggest that on average 29% of N fertilizer was in the soil after one year. In this chapter, the fertilizer application and N deposition accounted for 71% of total N input. Excessive N input by fertilizer application and N deposition could increase the storage of N in the soils. A future study will focus on the source of accumulation N in the soils.

## 2.5 Conclusion

This chapter presented the first spatially distributed total N budget across Great Britain and revealed the spatial pattern of N accumulation and loss. GB represents a net source of -1045±244 $\times 10^3$ tonnes N/yr(95% confidence interval). The total N budget at the 1 km$^2$ scale across GB ranged from -21±3 tonnes N/yr to 34±5 tonnes N/km$^2$/yr(95% confidence interval). Specifically, 66% of GB grid squares were source areas that export N to the surrounding atmospheric and marine environment, and 34% of GB was identified as sink areas that are accumulating total N. Sink areas were dominantly in western GB and source areas of total N were pre-

dominantly in eastern GB. For different land uses, 97% of urban areas and 98.5% of arable land use were sources of total N, while 34% of grassland was a net sink of total N.

**Table 2.6:** The percentage of inputs and outputs in the different N pathways of different countries.

| | N pathway | South Korea[1] | New Zealand[2] | China[3] | Northeaster U.S.A[4] | GB[5] |
|---|---|---|---|---|---|---|
| N input | BNF | 13% | 60% | 20% | 30% | 18% |
| | N deposition | 8% | 16% | 24% | 38% | 11% |
| | Net food and feed import | 24% | 0% | 3% | 16% | 11% |
| | Fertilizer | 55% | 24% | 53% | 16% | 60% |
| N output | Atmospheric N emission | 29% | 22% | 24% | 3% | 22% |
| | Fluvial N loss | 40% | 32% | 18% | 22% | 48% |
| | Denitrification and soil stored | 31% | 31% | 58% | 75% | 5% |
| | Net food and feed export | 0% | 15% | 0% | 0% | 0% |
| | Other N pathways[6] | 0% | 0% | 0% | 0% | 25% |

Source 1. Bashkin et al. (2002), 2. Parfitt et al. (2006), 3. Ti et al. (2012), 4. Van Breeman et al. (2002), 5. Data derived in this chapter. 6. Other N pathways considered in this study only, which included direct sewage N loss, N loss from groundwater, N gas emission from sewage treatment plants, industrial N emission and crop N remove.

# Chapter 3

# Spatial variability in the Trent catchment nitrogen budget: Identifying areas of nitrogen accumulation

## 3.1 Introduction:

N budgets can aid understanding of N flux dynamics at a range of scales (i.e. farm, regional, national, and global) (Van Breemen et al. 2002; Van Drecht et al. 2003; Hayakawa et al. 2009; Worrall et al. 2016a). Small-scale (refers to small measurement units and providing detailed information) studies (e.g. at the farm-scale) enable more detailed datasets that improve the accuracy of N flux estimates and enhance understanding of human impacts on the N cycle. In catchments, anthro-

pogenic inputs of N routinely exceed measured outputs leading to a large apparent N accumulation, especially for agricultural watersheds (Xing and Zhu 2002; Billen et al. 2009; Worrall et al. 2015). Trent catchment is an important agricultural region in the GB with 70% of land use dedicated to agriculture. In Chapter 2, the total spatial N budget for 2015 in GB was constructed revealing that the Trent catchment consisted both of N sink (N accumulation) and source areas (N loss). While N accumulation areas identified in Chapter 2 already considered all possible N pathways but it still does not resolve where in reality the N accumulation might be occurring (the accumulation occurs in topsoil or subsoil). This chapter presents the results of detailed local monitoring used to construct a watershed scale N budget for the Trent catchment revealing where N accumulates and leaves the catchment. Previous studies have shown that the potential for increased N storage occurred in soils (Fenn et al. 1998; Smil 1999; Leip et al. 2011). For example, Fenn et al. (1998) estimated N sequestration in forested soils occurred at a rate of 0.5 tonnes N/km$^2$/yr from 1996 to 1998. Leip et al. (2011) estimated the soil N budget of European and found annual accumulation of N in organic and inorganic form occurred in agricultural soils on the order of 15% - 20% of total N inputs. The accumulation of N somewhere in the terrestrial biosphere was demonstrated in Chapter 2 (the N spatial map showed N sink and source areas), however, a major part of the terrestrial biosphere which could not be observed were the subsoils. Therefore, this chapter hypothesises that N accumulation occurs in the subsoils of catchments. Van Meter et al. (2016) used resampling to calculate present-day total N in Iowa and Illinois compared to the total N at the same location in the mid-1990s and found evidence of N accumulation

in the landscape. In this chapter, due to lack of temporally-resolved soil data (the long history of soil data) across the Trent catchment, the C/N ratio of soil organic matter was used to assess where N accumulation was occurring. The C/N ratio is the ratio of total C and total N in the soil and a good indicator of the statue of soil nutrients as the change C/N ratio related with the status of nutrients (Tian et al. 2010). A high C/N ratio (larger than 25 on a mass basis) could increase immobilization process that indicates that organic matter is accumulating faster than it is decomposing (Fazhu et al. 2015). The change in the soil C/N ratio also can be used to explain the status (loss or accumulation) of C and N stock in the soil. Therefore, a change in the C/N ratio can be considered as a necessary condition for N accumulation or loss.

Chapter 3 is divided into 2 sections: the first section estimates the N budget of the Trent catchment, optimising the spatial N budget of GB by incorporating local N flux information; the second section uses the estimated Trent catchment N budget to target soil sampling in an effort to understand if and where N accumulation is occurring. Overall, the objectives of this study were, therefore, to determine the distribution of N sink and source areas for the Trent catchment using a spatially differentiated total N budget created in this chapter, and to use the budget maps to guide a field sampling exercise to assess whether or not N accumulation has occurred in the subsoil.

## 3.2 Approach and Methodology

Temporally-resolved data for the N content of soils is rare. Due to the lack of temporally-resolved soil data across catchments, the approach of this chapter was to identify areas of accumulation and sink using a spatially differentiated total N budget. On the basis of the constructed spatially-differentiated total N budget, areas of accumulation and loss under different land uses were compared by analysing the C/N ratio of their soil profiles. The hypothesis of this chapter is that N accumulation occurs in the subsoils of catchments. The expected result was that the two-way interaction term between N status and soil depth would be significant and in which case the C/N ratio should be lower at depth in the sink areas compared to source areas. If supported by the data, this would suggest N accumulation in the subsoil.

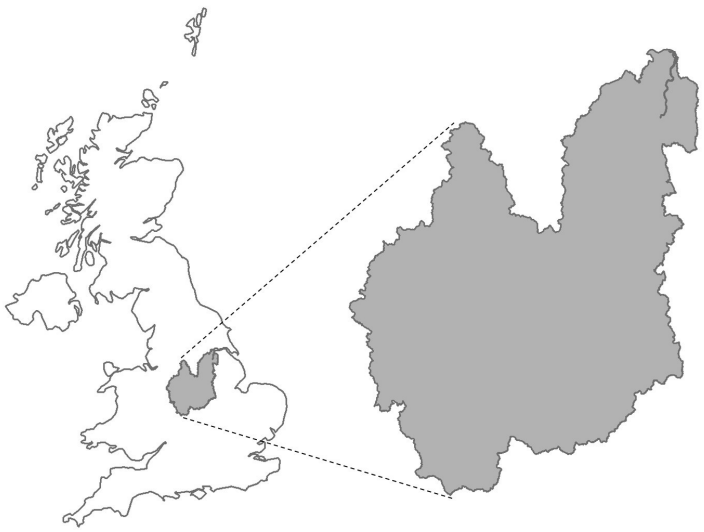

**Figure 3.1:** Location and outline of the River Trent catchment.

### 3.2.1 Data and study area

The River Trent is the third-longest river in the UK, flowing from its source above Stoke-on-Trent to the Humber Estuary (Figure 3.1). The Trent catchment, including all of the River Trent's tributaries, covers an area of 8,231 $km^2$. It is an important agricultural region in the UK with 70% of land use dedicated to agriculture. The most intensive mixed farming occurs at the centre of the Trent catchment. Urban areas comprise 30% of the catchment including the cities of Birmingham, Nottingham, Derby, Leicester, Burton-on-Trent, Stoke-on-Trent, Stafford, Cannock and Lichfield with approximately six million people residing in the catchment. As a study area, the Trent catchment has several advantages including: i) very long records of surface and groundwater quality; ii) the catchment is known to consist of both N sink and source areas (Figure 3.2); and iii) land use and soil type vary considerably across the catchment.

In Chapter 2, the spatial N budget of Great Britain (GB) was constructed based on national scale N fluxes that identified the distribution of sink areas and source areas across the whole of GB (Figure 3.2). While catchment-scale N activity flux data presented in Chapter 2 are sufficiently resolved for a national-scale study, herein more detailed local monitoring data (river discharge and concentration data) were used to estimate N fluxes (fluvial N loss and groundwater N loss) and optimise the accuracy of the catchment-scale spatial N budget by estimating local monitoring data. Within this chapter estimates for BNF, N fertiliser input, atmospheric N deposition input, food and feed transfer, atmospheric N emission and denitrification were taken from Chapter 2 whilst estimates for groundwater N loss (N losses to groundwater)

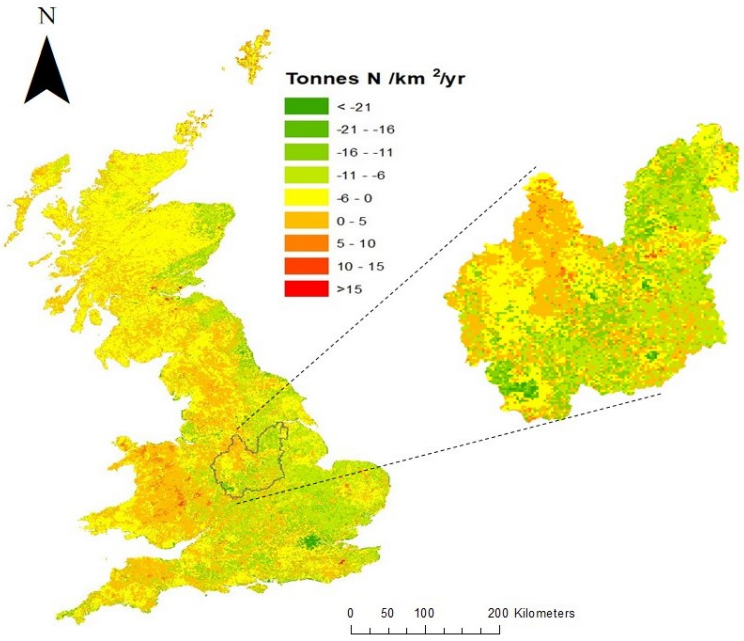


**Figure 3.2:** The spatial total N budget for GB and outline of Trent catchment in total N budget.

and fluvial N loss were refined with data specific to the Trent catchment.

For the Trent catchment, local surface water quality data were used to calculate total fluvial N flux ($NO_3^-$, $NO_2^-$, $NH_4^+$, DON and PON). The data for $NO_3^-$, $NO_2^-$ and $NH_4^+$ were obtained from the Environment Agency (`http://environment.data.gov.uk`). Environment Agency did not directly measured concentrations of DON and PON, however, the former can be estimated from measured dissolved organic carbon (DOC) based on the average C/N ratio (8.1) (Hillier 2001). Hillier (2001) also reported that the organic carbon content of organic matter is between 45% and 50%, the POM flux was estimated by suspended sediment, mineral concentration and river flow date, thus it is possible to estimate the POC and PON based on the average C/N ratio (8.1) of suspended sediment and suspended sediment concentrations are monitored by the Environment Agency.

For every Trent sub-catchment (Figure 3.3), fluxes of dissolved N species could be calculated using N species concentration and discharge data. Daily river discharge data were available from the National River Flow Archive (NRFA;https://nrfa.ceh.ac.uk). To calculate the N species flux of each Trent sub-catchment, only sites for which concentration matched with discharge data were used. The approach to the calculation of annual N flux used here was the same as that used by Worrall et al. (2012a) for the dissolved N flux from the UK, which the annual flux at the site was estimated by the measured concentration at the site and river discharge based on the data from 2005 to 2015.

Only catchment physical characteristics (soil and land use), which have a physical interpretation with respect to fluvial N export and could be mapped across the Trent catchment were considered here. Land use was classified into arable, grass and urban based on classification systems of the June Agricultural Census for 2004 (Defra, 2005), and, the soil was classified into mineral, organo-mineral and organic soil based on the classification system of Hodgson (1997). So as to map fluvial N losses across the entire catchment, the multiple linear regression was used to compared flux of each determinand to the physical characteristics of each sub-catchment. The regression model between catchment characteristics (land use, soil type) and measured fluvial flux was constructed in this chapter. And, the regression was used to assess the relationship between average flux and catchment characteristics. Therefore, the relationship between land use, soil type and N fluvial flux can be used to model the N fluvial losses for all cells as land use and soil type are available for each grid cell. Moreover, the determinand flux was predicted as a function of sub-catchment

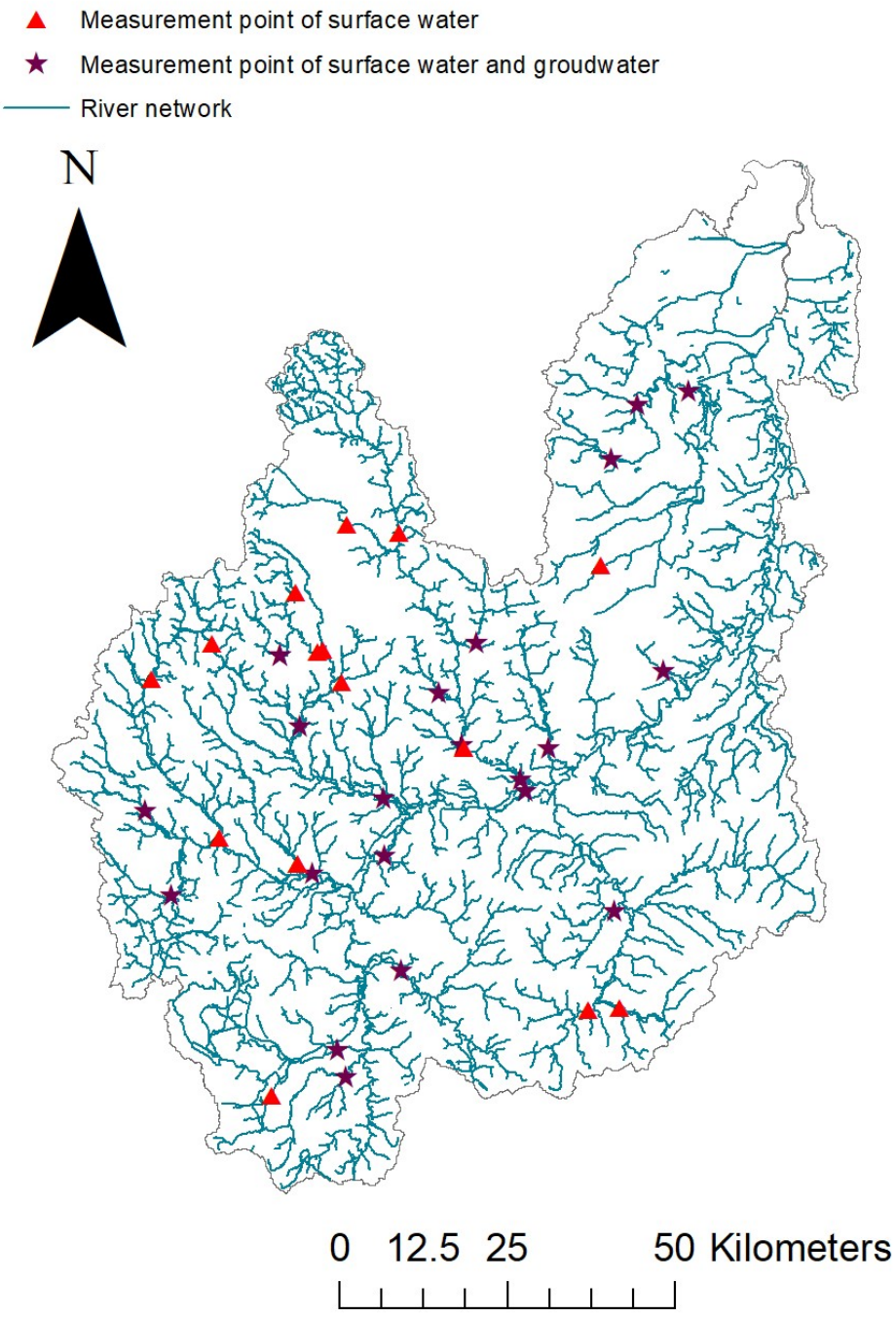


**Figure 3.3:** The location of sites where estimated N species flux could be calculated. Purple stars denote where N species fluxes in surface water and ground water were calculated and, red triangles denote where only N species flux in surface water were calculated.

soil and land use which can be directly mapped across the Trent catchment. This improved the accuracy of the fluvial N flux pathway in the N budget compared to the national scale fluvial flux estimates.

N flux to groundwater was labelled as a loss from the terrestrial biosphere to groundwater in this thesis. The nitrogen recharging to groundwater may well eventually return to the river and be included in estimating the N flux from soil to the river where baseflow discharges to the river system at the tidal limit. Groundwater represents a significant source or sink if the concentration of N in the groundwater is changing. Stuart et al. (2007) have shown a significant increase in concentration in GB groundwater over recent decades thus, groundwater loss can be calculated by the N concentration and storage in the aquifer. The N from baseflow discharge to the river system was calculated in the N fluvial flux pathway. For improved accuracy of net groundwater N flux, local monthly rainfall amount, daylight hours, and air temperature data were obtained from the UK Met Office (`https://www.metoffice.gov.uk`). The groundwater N loss pathway was estimated as the difference between meteorological rainfall data and actual evapotranspiration (AET) data. The AET was calculated using daylight hours, length of days and air temperature based on the Grindley model (Grindley 1970). The concentration data for $NO_3^-$,$NO_2^-$ and $NH_4^+$ of groundwater also were obtained from the Environment Agency (`http://environment.data.gov.uk`). The multiple linear regression was used to determine the relationship between the average N species flux to groundwater and catchment characteristics (land use and soil type). Then, the determinand flux of groundwater was predicted by land use and soil type using this

regression model.

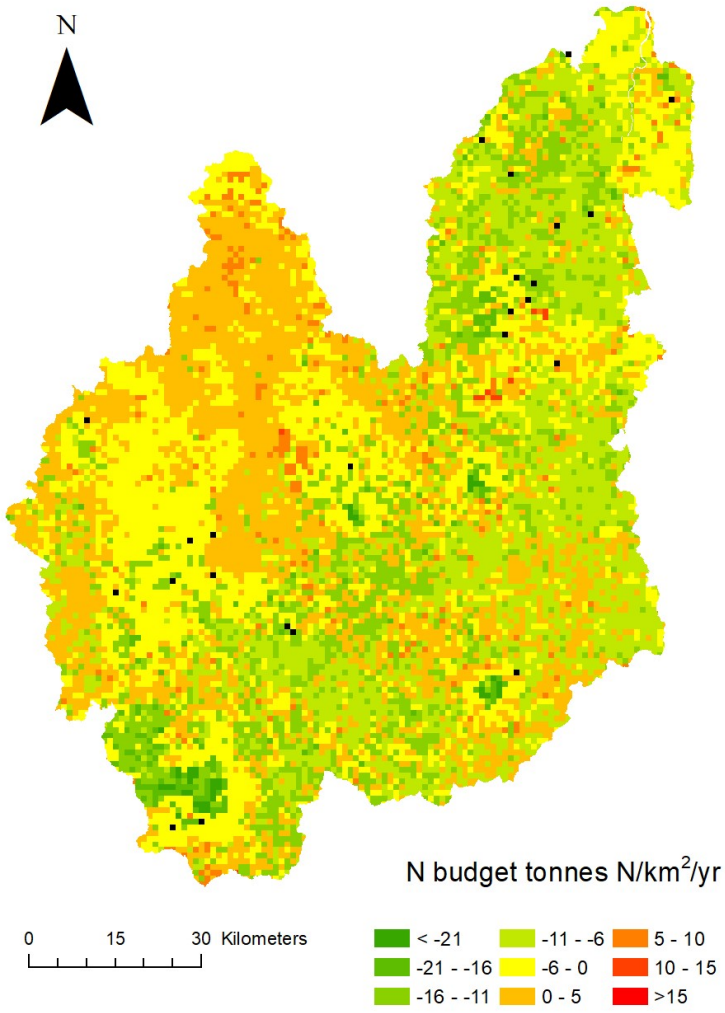


**Figure 3.4:** The spatial N budget of the Trent catchment and 24 soil sampling locations (black squares denote the location of sampling and the cell size is 1 km$^2$)

### 3.2.2 Field sampling and C/N ratio

To test the hypothesis that N accumulation occurs in the subsoil, the greatest contrast (i.e. henceforward referred to as endmembers) between areas of predicted sink and source were selected from the spatial terrestrial N budget derived for the Trent catchment. To get a statistically representative dataset, 24 locations were chosen

based upon the total N budget map (Figure 3.4). Three locations were selected from each combination of three factors: soil type (mineral and organo-mineral soils – organic soils were not included as they never showed a contrast in their N accumulation status); land uses (arable and grassland); and accumulation status (sink or source). Two levels of each of three factors were selected with each sampled in triplicate gave rise to 24 sample locations (Figure 3.4). Site-specific soil data were collected for all 24 locations. The site-specific soil data were identified and extracted from soil map series. Land use at each of the 24 locations was identified from land cover data. Additionally, each of 24 sample locations was identified as arable or grassland based on appearance in the field and confirmation by the landowner when interviewed.

At each of the 24 locations, two replicate soil cores were taken using a 6 cm gouge corer, and each core is 0.5 meters. Each core was subdivided into 4 samples based on soil profiles (two in the plough layer and two in the subsoil) resulting in a total of 192 soil samples. It was difficult to distinguish between topsoil and subsoil in same cores, and these soil cores were subdivided into more than 4 samples. Therefore, the total number of soil samples was 213. Samples were subdivided in the field and the sample name, date, location and depth recorded. Prior to shipping, samples were air dried (by not sealed bag) to reduce the moisture content. In the laboratory, all samples were dried to 105°C overnight in an oven to remove remaining moisture. The dried sample was sub-sampled and a portion taken for loss on ignition (LOI) analysis. The LOI was measured as the mass loss between the sampled dried at 105°C and the mass of the sample after 4 hours at 550°C. A second sub-sample

was freeze dried, ball milled, and weighed into 20 mg tin containers for analysis on Thermo Scientific Flash 2000 Organic Elemental Analyser and NC (Nitrogen Carbon) Soil Analyser. This instrument is based on the process of dynamic flash combustion for the determination of carbon, hydrogen, nitrogen, sulphur and oxygen in solid samples. This instrument has a detection limit of 0.5%, which is the lowest quantity of a substance that can be distinguished from the absence of that substance (blank value) with a stated confidence level (99%). The C and N concentration of each sample was then used to calculate the C/N ratio.

### 3.2.3 Statistical analysis

This experiment was designed as a four-factor analysis of variance (ANOVA) with C/N as the response variable. The first factor considered was the accumulation status (henceforward referred to as Status) as identified from the calculated total N budget, this had two levels - sink and source. The second factor considered was soil depth (henceforward referred to as Depth) which could be divided into two levels – topsoil and subsoil. Thirdly, soil types (henceforward referred to as Soil) which had two levels – mineral and organo-mineral (OrgMin). Fourthly, land use (henceforward referred to as Land use) which also had two levels – grass and arable. Given the nature of the experimental design, it was possible to consider two-way interactions and three-way interactions between these factors. The hypothesis (subsoil C/N ratio is significantly lower than the C/N ratio in the subsoil of areas identified as being of net total N loss) was tested by interaction term not by the single factor, and the expected result was that the two-way interaction term between Status and Depth

would be significant and in which case the C/N ratio should be lower at depth in the sink areas compared to source areas. If supported by the data, this would suggest N accumulation in the subsoil. The C/N ratio is a necessary but not sufficient condition for this hypothesis. The ANOVA was also performed on C content and N content separately. In addition, LOI data was included in the ANOVA statistical analysis as a covariate in case there was an effect on the distribution of C and N content with the organic matter content.

Before any ANOVA was performed, the data were Box-Cox transformed to remove outliers and tested for normality using the Anderson-Darling test (Anderson et al. 1952). If necessary the data were log-transformed and re-analysed. The homogeneity of the variance was tested using the Levene test. The magnitude of the effects of each significant factor and interaction was calculated using the generalised $\omega^2$ (Olejnik and Algina 2003) and values were presented as least-square means (otherwise known as marginal means). Post hoc assessment of factors and interactions was carried out using the Tukey test and, unless otherwise stated, statements of significance refer to the effect being different, or not, from zero at the probability of 95%. Power analysis was used post hoc to estimate the achieved power within the dataset. The power analysis was performed using the GPower 3.1 software (Faul et al. 2007; `http://gpower.hhu.de/`). A priori the acceptable power was set at 0.8 (a false negative probability $\beta$= 0.2). In this study, df = equal to 1, n = 220 was assumed, the significance was 95% and the required experimental power was set at 95%.

## 3.3 Results

### 3.3.1 Fluvial N loss

The DON flux could be calculated for 19 Trent sub-catchments with complete land use and soil type data using estimated DOC flux (which estimated by concentration date and river discharge). The best-fit regression equation ($R^2 = 0.92$, df = 18) for DON was:

$$DON_{flux} = \underset{(0.09)}{0.49}\,Arable + \underset{(0.06)}{0.20}\,Grass + \underset{(0.08)}{0.32}\,Urban \tag{3.1}$$

Where, $DON_{flux}$ is the average annual DON flux in tonnes N $yr^{-1}$, *Arable* is the area of arable land in $km^2$, *Urban* is the area of urban land use in $km^2$, *Grass* is the area of grassland in $km^2$, and the numbers in the brackets are standard error of each coefficient. Note there is no constant term in Eq.(3.1) as it was found not to be significantly different from zero at a 95% probability. For nitrate ($NO_3^-$) flux, a total of 28 sub-catchments could be considered. The best-fit equation ($R^2 = 0.94$, df = 27) for nitrate flux was:

$$Nitrate_{flux} = \underset{(2.27)}{9.199}\,Arable + \underset{(2.58)}{10.71}\,Grass + \underset{(2.45)}{9.94}\,Urban - \underset{(2.13)}{6.27}\,Area. \tag{3.2}$$

Where, $Nitrate_{flux}$ is the average annual nitrate flux in tonnes N $yr^{-1}$ and *Area* is the area of whole catchment in $km^2$. All other variables are as defined for Eq. (3.1) above.

With respect to ammonium ($NH_4^+$) N flux, a total of 33 sub-catchments were

considered and the best-fit equation ($R^2$ =0.52, df=32) determined to be:

$$NH^{+}_{4flux} = \underset{(0.04)}{0.20}\,Grass + \underset{(0.18)}{0.41}\,Urban - \underset{(0.07)}{0.24}\,Mineral. \tag{3.3}$$

Where $NH^{+}_{4\,flux}$ is the average annual $NH^{+}_{4}$ N flux in tonnes N $yr^{-1}$ and *Mineral* is the area of mineral soil in $km^2$. All other terms are as defined for Eq. (3.1) above. The PON flux could be calculated using data available from 20 Trent sub-catchments. The best-fit equation ($R^2$=0.91, df=19) was:

$$PON_{flux} = \underset{(0.02)}{0.12}\,Grass + \underset{(0.01)}{0.09}\,Urban \tag{3.4}$$

Where $PON_{flux}$ is the average annual PON flux in tonnes N $yr^{-1}$. All other terms are as defined for Eq. (3.1) above.

### 3.3.2 Groundwater N loss

The DOC flux loss to groundwater was estimated by concentration data and river discharge data. After estimated DOC flux, the DON flux could be calculated for 22 sub-catchments with complete land use and soil data. The best-fit regression equation ($R^2$=0.93, df=21) for DON was:

$$DON_{groundwater} = \underset{(0.01)}{0.03}\,Grass + \underset{(0.01)}{0.08}\,Urban \tag{3.5}$$

Where: $DON_{groundwater}$ is the average annual DON flux (tonnes N $yr^{-1}$) loss to groundwater. All other terms are as defined above.

A total of 22 sub-catchments were considered in the analysis of nitrate. The best-fits equation ($R^2$=0.95, df=21) for nitrate flux was:

$$Nitrate_{groundwater} = \underset{(0.19)}{1.32}\,Mineral + \underset{(0.33)}{1.33}\,OrgMin \tag{3.6}$$

Where: $Nitrate_{groundwater}$ is the average annual nitrate flux (tonnes N $yr^{-1}$) loss to groundwater; *OrgMin* is the area of OrgMin soil ($km^2$). All other terms are as defined above.

Groundwater $NH_4^+$ flux could be considered in 22 sub-catchments. The best-fit regression equation ($R^2$=0.95, n = 22) for $NH_4^+$ groundwater flux was:

$$NH^+_{4groundwater} = \underset{(0.03)}{0.04}\,Urban + \underset{(0.01)}{0.03}\,OrgMin + \underset{(0.01)}{0.07}\,Organic. \tag{3.7}$$

Where: $NH^+_{4\,groundwater}$ is the average annual $NH_4^+$ flux (tonnes N $yr^{-1}$) loss to groundwater; and *organic* is the area of organic soil in the catchment ($km^2$). All other terms are as defined above.

### 3.3.3 Spatial N budget of the Trent catchment

Estimates of each of N input and output flux for the entire Trent catchment in 2015 are given in Table 3.1, and the spatial N distribution across the Trent catchment is shown in Figure 3.4. Chemical fertilizer N application was the largest N input into the Trent catchment, accounting for 64% of the total N input in 2015. Due to variations in fertilizer applications for crops and grass, the broad flat plains located in the east of the Trent catchment had the highest fertilizer inputs (14±2 tonnes/$km^2$/yr, where the value given is the mean and standard error). Fertilizer inputs are shows in Figure 3.5 and Figure 3.13 shows the distribution of land use across the Trent catchment. Conversely, the Peak District National Park area, which is located in the northwest of the Trent catchment, had lower fertilizer input (4±1 tonnes/$km^2$/yr) compared to other crop and grass areas (Figure 3.5 and 3.13). The total BNF was 19±3 $\times 10^3$ tonnes N/yr, which accounted for 17% of the total N

inputs. The BNF input to grass was higher than to bean and peas. Thus, the highest BNF input (compared to other land uses) was observed for grass areas such as Peak District national park area (Figure 3.6 and 3.13). Total atmospheric deposition input to the Trent catchment was 16±2 $\times 10^3$ tonnes N/yr which accounted for 14% of total N input. The gaseous form of N can migrate over a long distance, and the deposition was not accounted to occur nearby the N gas source. The distribution of atmospheric deposition shown in Figure 3.7. Net N input through food and feed transfer was 8±3 $\times 10^3$ tonnes N/yr, it contributed 7% of total N input. The Trent catchment is an agricultural region, and hence food produced in Trent catchment is adequate to meet the demand of that population, and therefore, large areas of the Trent catchment showed a net N output though food and feed transfer. The distribution of net food and feed transfer is shown in Figure 3.8.

Atmospheric N emissions included NO, $N_2O$ from agricultural land and, $NH_3$ from livestock and fertilizer. The amount of atmospheric N emission was 47±13 $\times 10^3$ tonnes N /yr, which accounted for approximately 55% of total N outputs. The highest atmospheric N emissions occurred in areas of the northwestern Trent catchment (Figure 3.9 and 3.13). The predicted fluvial N loss at soil source was 28±13 $\times 10^3$ tonnes N /yr which accounted for about 28% of total N outputs. There was a large fluvial flux loss (N loss to river) in the western Trent catchment (Figure 3.10 and 3.13). The total amount of denitrification was 9±4 $\times 10^3$ tonnes N/yr. 11% of the total N output was predicted to come from denitrification. The highest denitrification output was found in the eastern part of the Trent catchment as the major land use there was arable (Figure 3.11 and 3.13). The northwest of the Trent

catchment had lower denitrification outputs than the eastern areas of the Trent catchment due to a land use dominated by forest and grass (Figure 3.11 and 3.13). Groundwater loss (N loss to groundwater) was the lowest output which accounted for 1% of total N output. The distribution of groundwater loss is shown in Figure 3.12.

**Table 3.1:** Summary of the calculated values of N inputs and outputs for Trent catchment in 2015; and proportions of N inputs or outputs in 2015.

| | Flux in 2015 ($10^3$ tonnes N/yr) | Proportions of N inputs/outputs |
|---|---|---|
| Input | | |
| Biological N fixation | 19 | 16% |
| Atmospheric deposition | 16 | 13% |
| Inorganic fertilizer | 76 | 64% |
| Net food and feed transfer | 8 | 7% |
| Sub-total | 119 | |
| Output | | |
| Atmospheric emission | 47 | 55% |
| Terrestrial denitrification | 9 | 11% |
| Fluvial loss at soil source | 28 | 33% |
| Ground water loss | 0.5 | 1% |
| Sub-total | 85 | |
| Total N budget | 35 | |

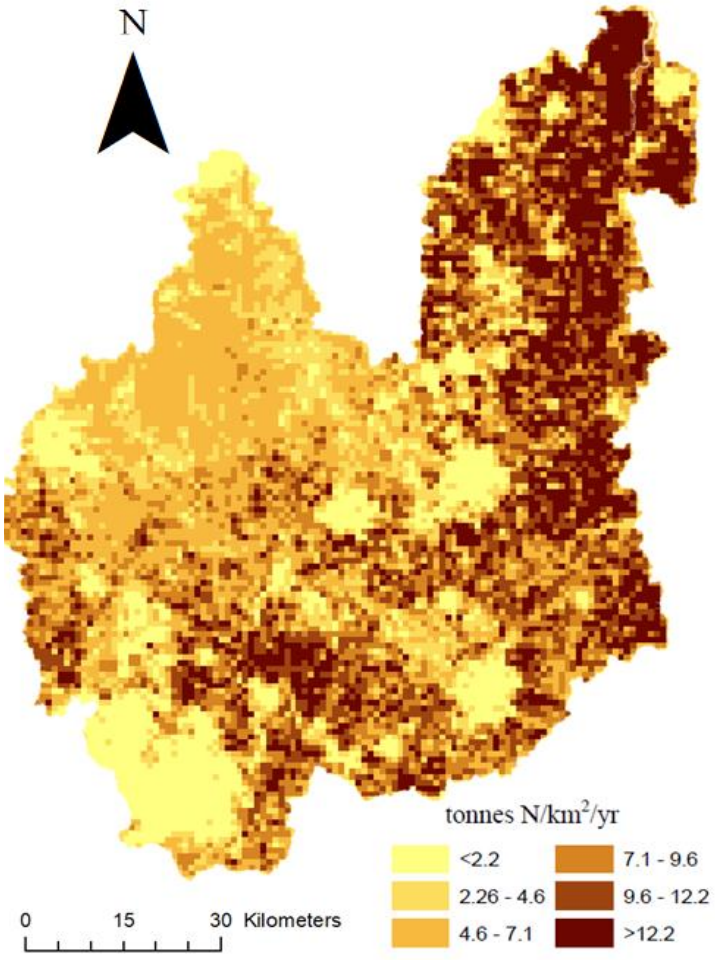


**Figure 3.5:** The predicted distribution of fertilizer input in the Trent catchment for 2015

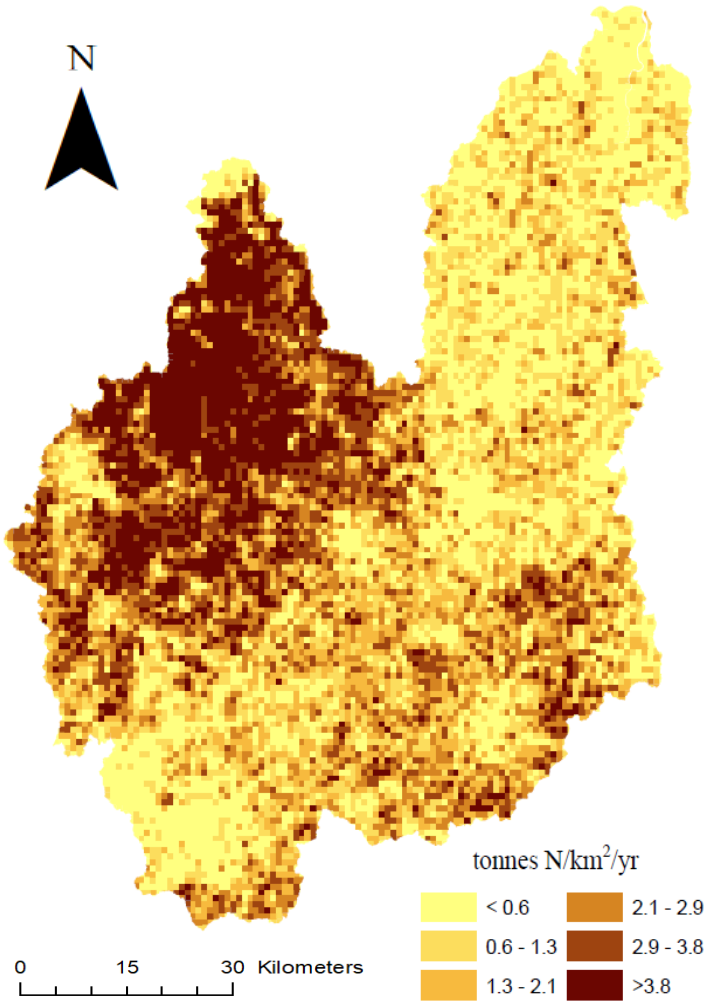


**Figure 3.6:** The predicted distribution of BNF in the Trent catchment for 2015

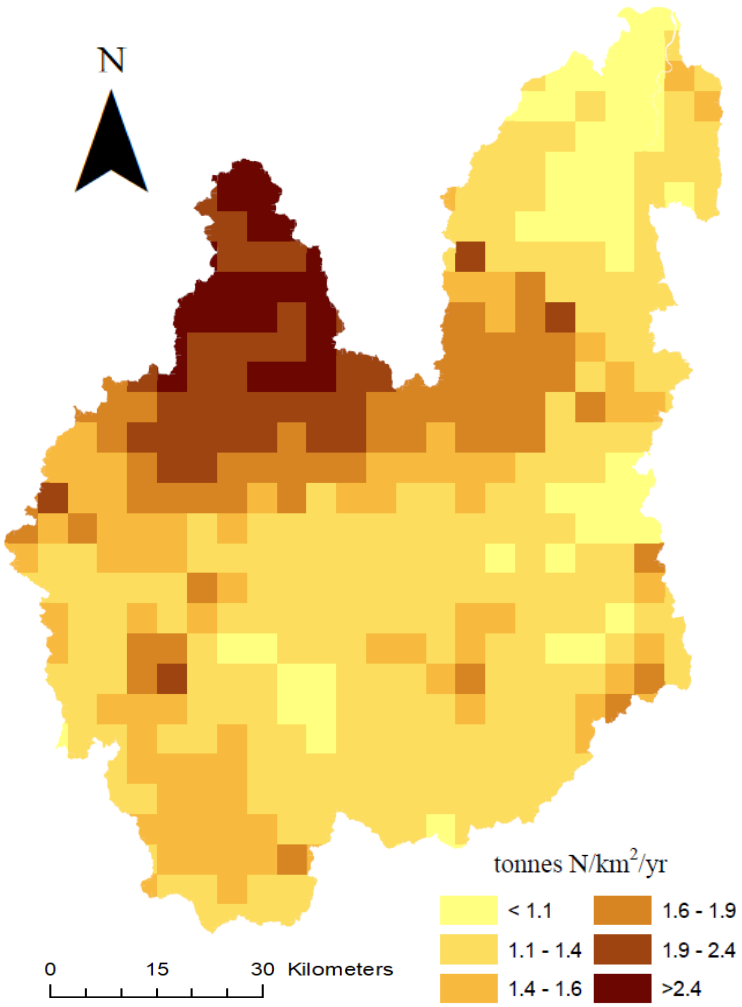


**Figure 3.7:** The predicted distribution of N deposition in Trent catchment for 2015

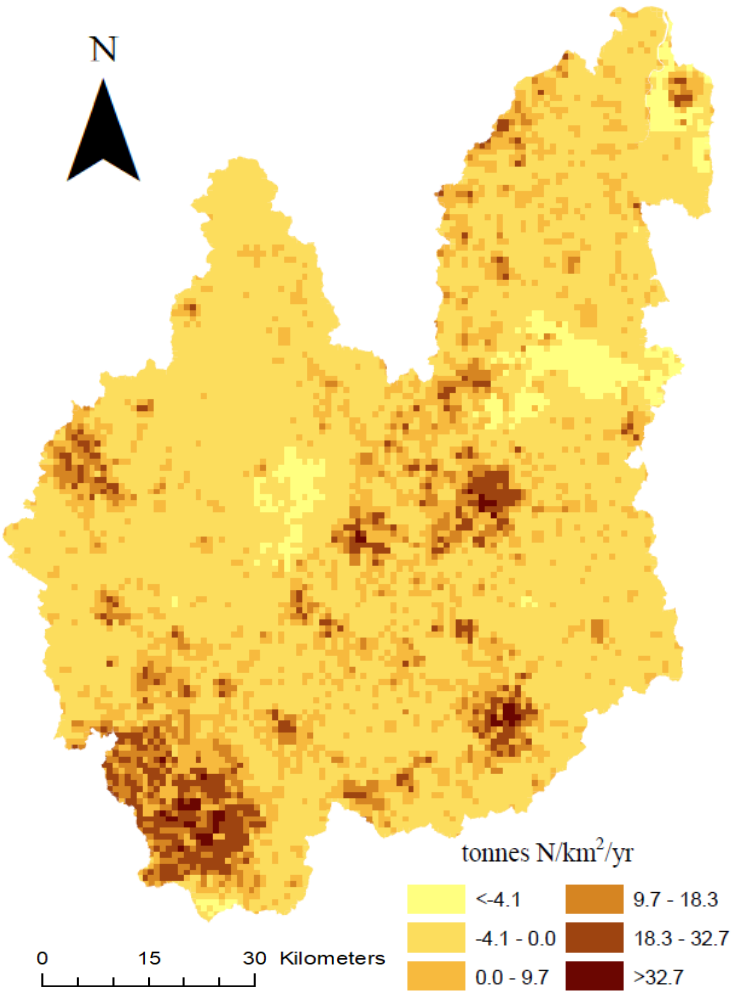


**Figure 3.8:** The predicted distribution of net food and feed transfer in the Trent catchment for 2015

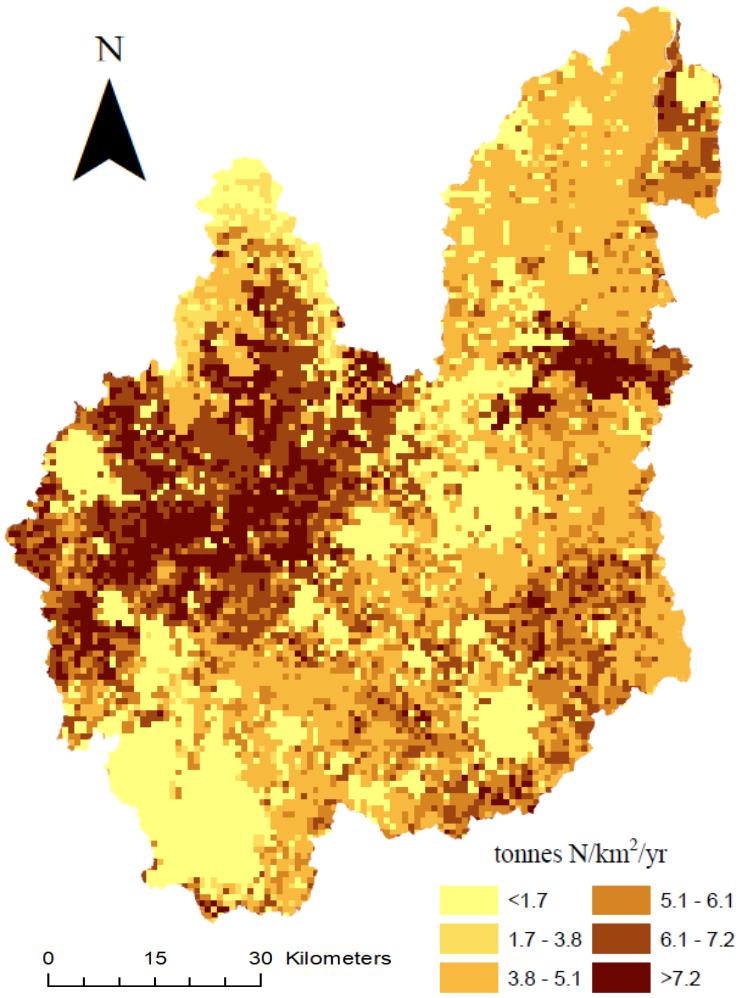


**Figure 3.9:** The predicted distribution of N gas emission in the Trent catchment for 2015

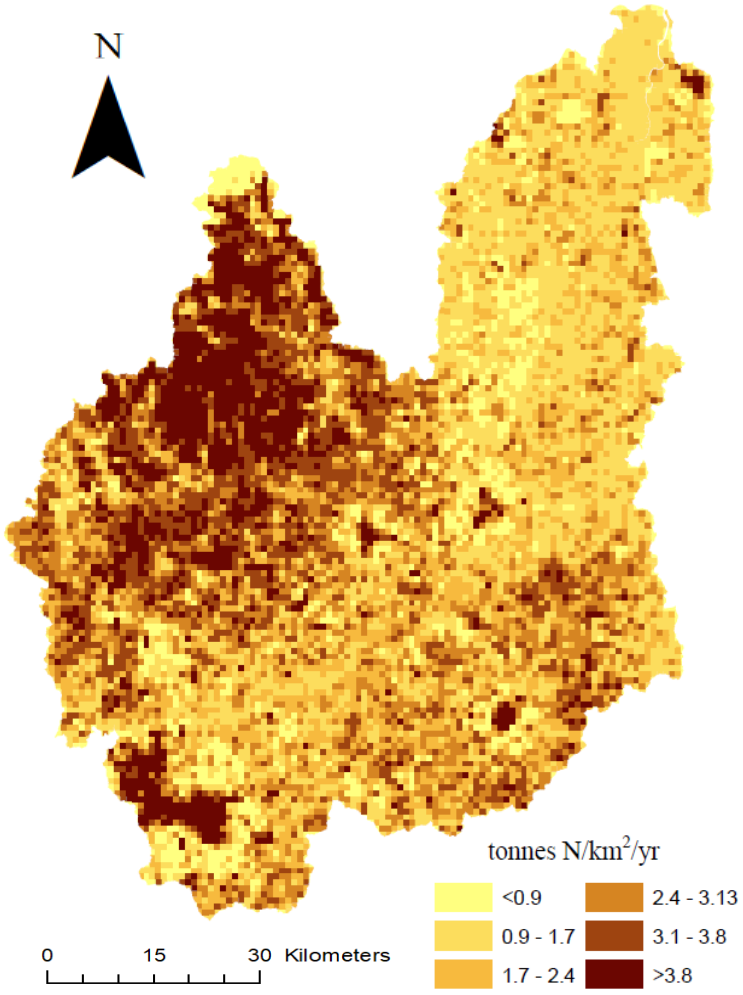


**Figure 3.10:** The predicted distribution of total N fluvial loss at soil source in the Trent catchment for 2015

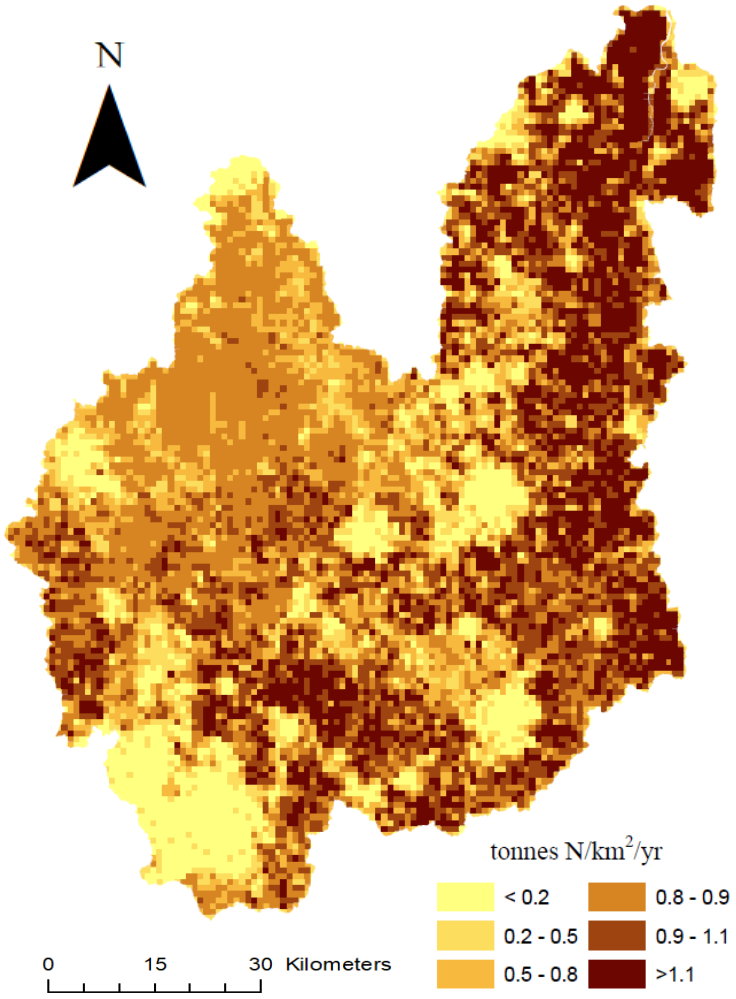


**Figure 3.11:** The predicted distribution of denitrification in the Trent catchment for 2015

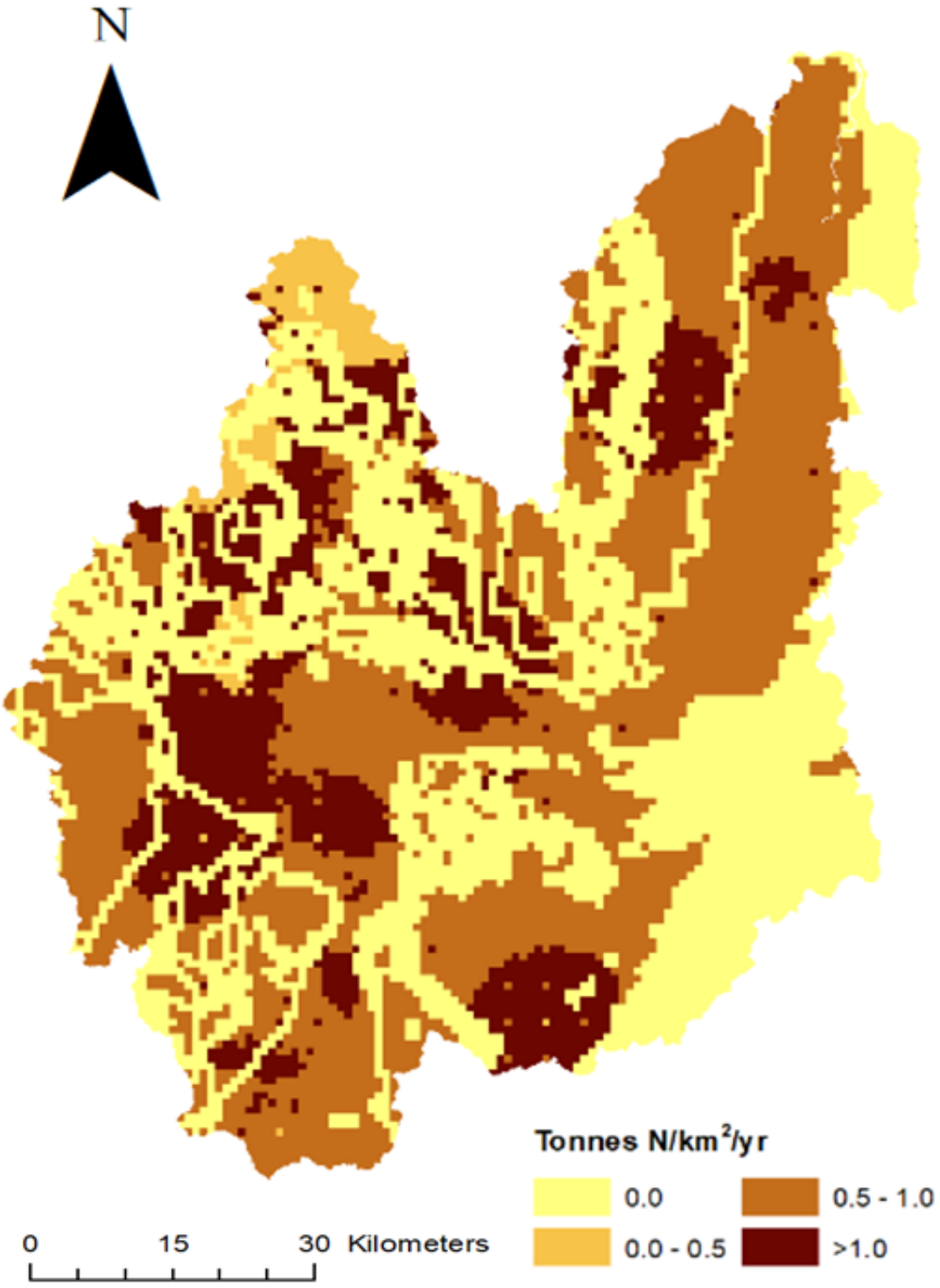


**Figure 3.12:** The predicted distribution of N loss from groundwater in the Trent catchment for 2015

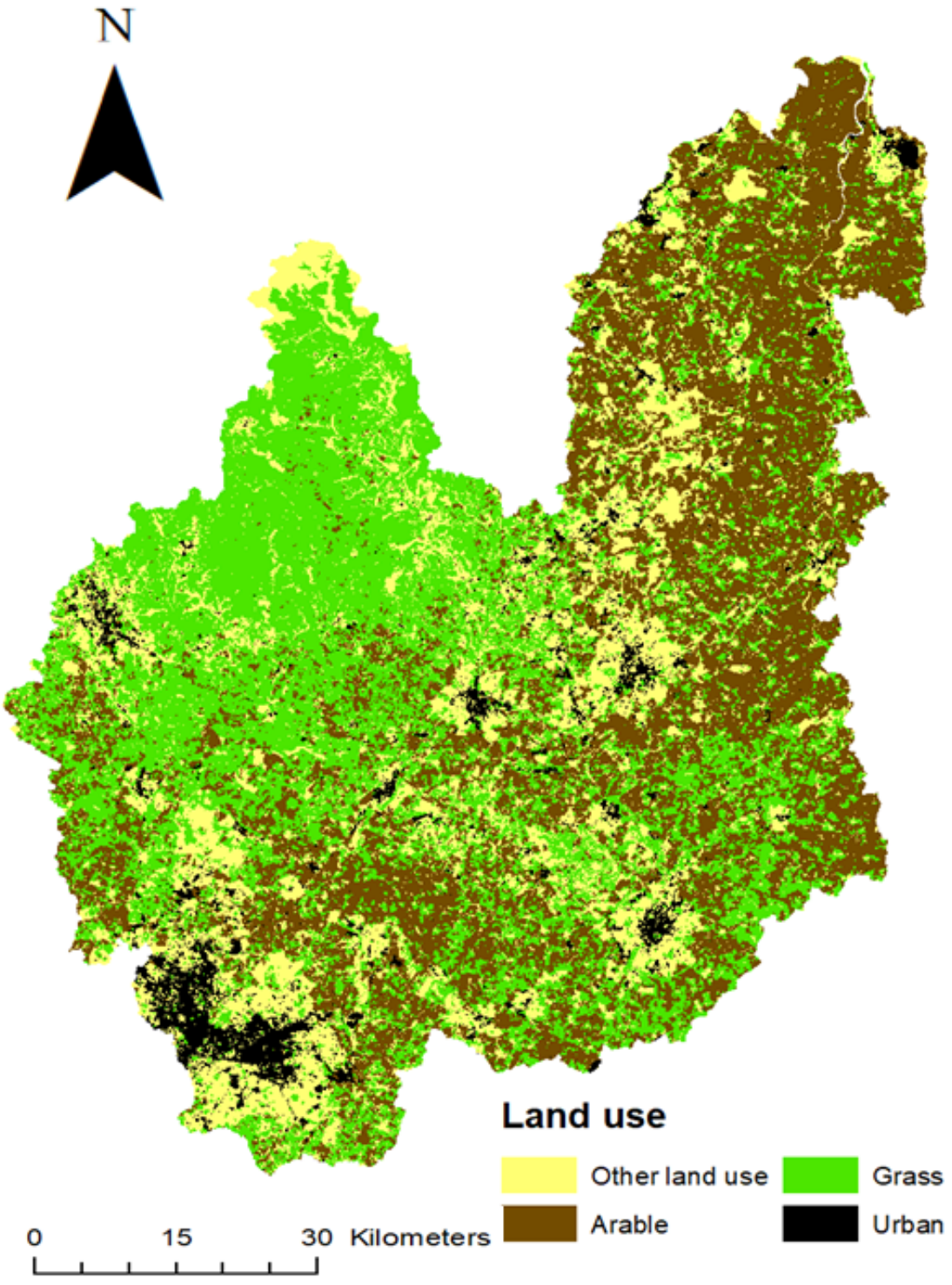


**Figure 3.13:** The distribution of land uses in the Trent catchment in 2015

Across the Trent catchment, 31% of total areas were source areas and 69% of total areas were sink areas. The source areas were mainly located in the northwest and central-south of the Trent catchment (Figure 3.4). The sink areas were mainly located in the southwest, northeast and the middle of the Trent catchment (Figure 3.4). The spatial distribution of 24 sampling points are shown in Figure 3.4 and the status shown in Table 3.2.

**Table 3.2:** The N accumulation status of the 24 soil sampling sites.

| | Land use/soil type | Status | latitude | longitude | number |
|---|---|---|---|---|---|
| 1 | Arable-mineral | Sink | 53°8′45.56” | −0°56′50.65” | 01-01 |
| 2 | Arable-mineral | Sink | 53°32′51.67” | −0°39′56.84” | 01-02 |
| 3 | Arable-mineral | Sink | 53°8′16.37” | −1°3′8.07” | 01-03 |
| 4 | Arable-mineral | Source | 53°37′51.66” | −0°54′18.45” | 01-04 |
| 5 | Arable-mineral | Source | 53°21′42.06” | −0°56′31.54” | 01-05 |
| 6 | Arable-mineral | Source | 53°26′36.86” | −1°3′37.83” | 01-06 |
| 7 | Arable-OrgMin | Sink | 53°19′24.70” | −0°43′4.20” | 02-01 |
| 8 | Arable-OrgMin | Sink | 53°14′43.76” | −1°1′11.62” | 02-02 |
| 9 | Arable-OrgMin | Sink | 53°11′31.34” | −1°4′51.54” | 02-03 |
| 10 | Arable-OrgMin | Source | 53°16′54.05” | −1°2′56.63” | 02-04 |
| 11 | Arable-OrgMin | Source | 53°13′40.35” | −1°3′54.85” | 02-05 |
| 12 | Arable-OrgMin | Source | 53°16′20.38” | −1°0′15.42” | 02-06 |
| 13 | Grass-OrgMin | Sink | 52°53′55.96” | −1°52′30.31” | 03-01 |
| 14 | Grass-OrgMin | Sink | 53°6′17.58” | −1°33′38.96” | 03-02 |

| | | | | | |
|---|---|---|---|---|---|
| 15 | Grass-OrgMin | Sink | 52°31′10.75” | −1°21′37.27” | 03-03 |
| 16 | Grass-OrgMin | Source | 52°48′32.54” | −1°56′58.27” | 03-04 |
| 17 | Grass-OrgMin | Source | 52°49′4.58” | −1°50′44.31” | 03-05 |
| 18 | Grass-OrgMin | Source | 52°52′18.97” | −1°54′17.56” | 03-06 |
| 19 | Grass-mineral | Sink | 53°30′26.16” | −1°9′52.73” | 04-01 |
| 20 | Grass-mineral | Sink | 53°3′38.24” | −2°10′22.97” | 04-02 |
| 21 | Grass-mineral | Sink | 53°13′37.69” | −0°58′31.34” | 04-03 |
| 22 | Grass-mineral | Source | 52°44′11.86” | −1°39′12.22” | 04-04 |
| 23 | Grass-mineral | Source | 52°52′51.11” | −1°50′43.51” | 04-05 |
| 24 | Grass-mineral | Source | 52°43′39.34” | −1°38′19.17” | 04-06 |

### 3.3.4 C/N ratio

A summary of the C/N ratio results for all soil samples in different land uses and soil types sampled across the Trent catchment is given in Figure 3.14 and Figure 3.15. The C/N ratio in all investigated soil samples measured in this chapter varied from 7.43 to 23.32 (the weight ratio of C and N). Specifically, C/N ratio in arable land use ranged from 8.63 to 23.32 (median~11.79) and was higher in subsoil than topsoil. C/N ratio in grassland use ranged from 7.43 to 20.70 (median~10.93) and was higher in subsoil than topsoil. For different soil types, C/N ratio in mineral soil ranged from 7.83 to 17.50 (median~11.01) and was lower in topsoil than subsoil. The C/N ratio in OrgMin soil ranged from 7.43 to 23.32 (median~11.77) and was lower in topsoil than subsoil. In sink areas, the C/N ratio ranged from 8.55 to 23.32 (median~11.12) and

was higher in topsoil than subsoil. In source areas, the C/N ratio ranged from 10.13 to 13.15 (median~11.61) and was lower in topsoil than subsoil. The biggest difference between factor levels was for the sample factor, that was between topsoil and subsoil. The difference between treatment levels for the other factors was considerably less than that due to differences between land uses and would suggest that this one large difference might be dominating the other factors (Table 3.3).

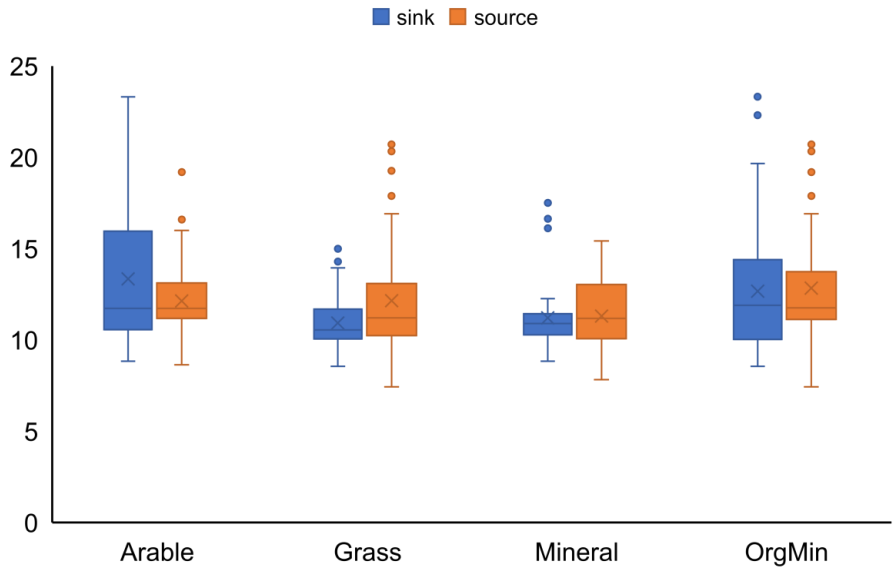


**Figure 3.14:** The C/N value of sink and source in different conditions.

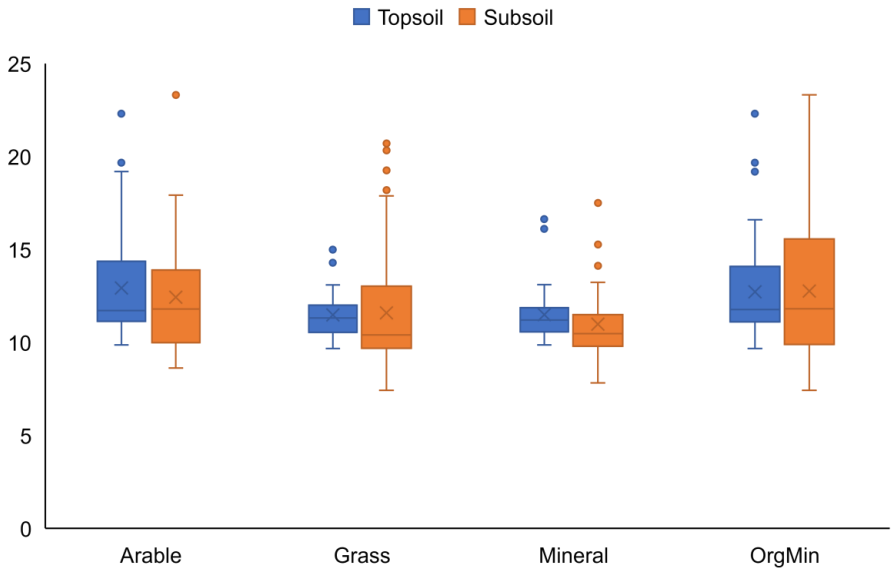


**Figure 3.15:** The C/N value of topsoil and subsoil in different conditions.

### 3.3.5 ANOVA

The data were Box-Cox transformed and no outliers were found. The C content, N content and C/N was tested by Anderson-Darling and showed the data (C, N and C/N) to be normally distributed. The power analysis suggested that this design was capable of detecting a difference between any of the levels greater than 0.55. The general linear model for the C/N ratio, without the inclusion of LOI as a covariate, explained 20.5% of the variance in the original dataset (Table 3.3). The largest effect on the data was the difference between land uses with the arable having C/N = 13.22±0.56 to that of grass 11.54±0.25 (values are given as mean and the standard error). The difference between arable and grass samples reflects significant

**Table 3.3:** The proportion of variance explained by each factor and interaction. Significant ($p<0.05$) factors or interactions are highlighted in bold.

| Source | C | N | C/N |
|---|---|---|---|
| Land use | **7.25** | **11.55** | **5.86** |
| Soil | **0.05** | **2.23** | **3.90** |
| Status | - | 0.29 | 0.00 |
| Depth | **15.19** | **17.68** | **0.13** |
| Land use * Soil | 0.07 | 0.03 | 0.01 |
| Land use * Status | 0.17 | 0.02 | **3.05** |
| Land use * Depth | **2.15** | **4.24** | 0.02 |
| Soil * Status | - | 0.03 | **2.20** |
| Soil * Depth | 0.90 | 0.84 | 0.00 |
| Status * Depth | 0.06 | 0.01 | 0.32 |
| Land use * Soil * Status | **3.85** | **3.41** | 0.27 |
| Land use * Soil * Depth | 0.05 | - | 0.52 |
| Land use * Status * Depth | 0.24 | 0.19 | **1.59** |
| Soil * Status * Depth | - | 0.13 | **1.97** |
| Land use * Soil * Status* Depth | 0.17 | 0.46 | 0.68 |
| Error | 65.13 | 58.89 | 79.50 |

differences for each element considered (C content and N content). The soil C/N under grassland was lower than under arable due to both lower C and higher N content in the soil under arable: land use explained 5.9% of the original variance

in the data set of C/N ratio. The second most important factor was that between mineral soil and OrgMin soil (3.9% - Table 3.3) with the mineral soil having C/N ratio = 11.72±0.52 compared to that of OrgMin with 12.75±0.33. The OrgMin soils have more organic matter than mineral soil. The mineral soil was found to have a lower C/N ratio than OrgMin soil due to both significantly lower C and higher N content in there soils. No other single factors (i.e.the Depth and Status factors) were found to have a significant effect on C/N ratio, there was no evidence that difference in the depth/status was leading to a significant change in C/N ratio. The main effects plot for C/N ratio is shown in Figure 3.16.

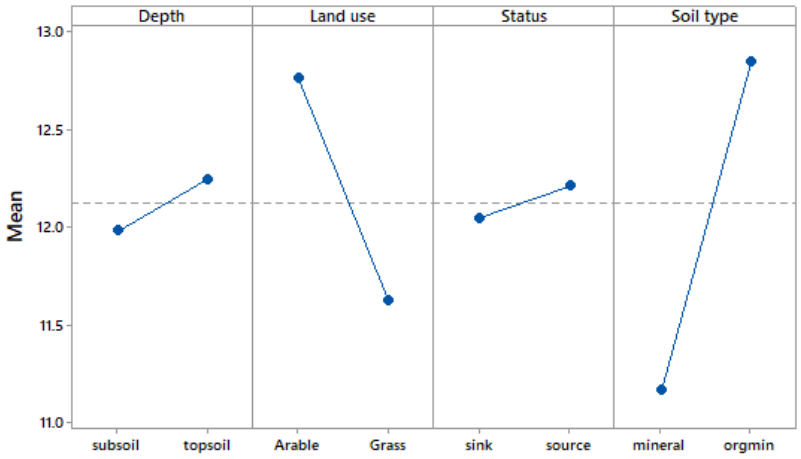


**Figure 3.16:** Main effects plot for C/N

A number of two-way interactions were significant. The most important interaction was that between the accumulation status and land use (explaining 3.1% of the original variance- Table 3.3). For sink areas, grassland use had a lower value of C/N ratio when compared to grassland on source areas. The second most important interaction was that between accumulation status and soil type (2.2% - Table 3.3). For sink areas, mineral soils had a lower C/N – a reduction of 0.2. In contrast, for

source areas, the presence of a mineral soil lead to a reduction in C/N by 0.15.

A number of three way interactions were found to explain considerable proportions of the original variance in the data. The highest proportion of the variance was explained by the interaction between soil types, accumulation status and depth – explaining 2.0%. Depth had the effect of lowering the C/N ratio when samples were collected from sink areas on OrgMin soils or source areas on mineral soils. The C/N ratio was significantly lower at depth for sink areas on OrgMin soil and significantly lower at depth for source areas on mineral soils. The least important, but still significant, three-way interaction (land uses, accumulation status and depth) was that of changing impact of depth (1.6% - Table 3.3). Depth had the effect of lowering the C/N ratio for samples collected from sink areas on grassland or source areas on arable. The C/N ratio was lower in the subsoil of sink areas compared to source areas under in grassland rather than arable land.

**Table 3.4:** The proportion of variance explained by each factor (including LOI as covariates) and interaction. Significant ($p<0.05$) factors or interactions are highlighted in bold.

| Source | C | N | C/N |
|---|---|---|---|
| LOI | **28.21** | **27.94** | **0.97** |
| Land use | - | 0.39 | **9.38** |
| Soil | 0.41 | - | **2.30** |
| Status | - | 0.01 | 0.01 |
| Depth | **1.94** | **2.84** | 0.19 |
| Land use * Soil | 0.01 | 0.05 | 0.02 |
| Land use * Status | 0.07 | 0.09 | **2.06** |
| Land use * Depth | 0.22 | **1.12** | 0.16 |
| Soil * Status | 0.02 | 0.07 | **2.91** |
| Soil * Depth | 0.19 | 0.16 | 0.04 |
| Status * Depth | - | 0.09 | 0.33 |
| Land use * Soil * Status | 0.46 | 0.33 | 0.11 |
| Land use * Soil * Depth | 0.02 | 0.01 | 0.51 |
| Land use * Status * Depth | 0.03 | 0.01 | **1.67** |
| Soil * Status * Depth | 0.04 | 0.25 | **1.60** |
| Land use * Soil * Status* Depth | 0.02 | 0.16 | 0.64 |
| Error | 68.28 | 66.47 | 77.09 |

To test N accumulation in the subsoil, the expected result was that the two-way interaction term between Status and Depth would be significant and in this case the C/N ratio should be lower at depth in the sink areas compared to the source areas. However, the two-way interaction term between Status and Depth was not significant. The three-way interaction term (Depth, Land use, and Status) suggested that depth has a significant effect upon C/N ratio between sink and source areas under grassland, i.e. this measure used to test for N accumulation did prove to be significant under grassland but not under arable.

The ANOVA was also performed including the LOI as a covariate. When the C/N ratio was considered, the LOI was a significant covariate, with C/N ratio increasing with LOI. In the ANOVA results, organic matter content had a significant effect (1.0% - Table 3.4). Adding covariates improved the fit of the model and affected the final results (variance explained by this model was larger than for the last model without LOI). Although this result was improved by the inclusion of a covariate no further factors, or interactions were found to be significant, likewise no factors or interactions, found to be significant without the covariates, proved to be insignificant with the inclusion of the covariate.

## 3.4 Discussion

The hypothesis was that the subsoil C/N ratio is significantly lower than the C/N ratio in the subsoil of areas identified as being of net total N loss. However, the result of ANOVA found that only data from grassland supported this hypothesis and arable land use did not fit this hypothesis. The fact that data from arable

land did not support the hypothesis can be explained by several reasons. Firstly, in addition to the factors included Land use, Soil and Status, studies show that C/N ratio also can be influenced by other factors such as soil condition included texture (Callesen et al. 2007) and climate (Miller et al. 2004). Callesen et al. (2007) found the C/N ratio has a positive relationship with the percentage of sand, with higher C/N ratio observed in coarse-textured soils. Miller et al. (2004) developed a C/N model that showed the C/N ratio increases with increasing mean precipitation and decreasing mean annual temperatures. Therefore, soil condition and climate potentially explain why arable did not fit the hypothesis. In addition, ploughing may be another reason why arable land was not in agreement with this hypothesis. Many farmers plough their arable land at least once a year as the crop rotation and maintain fertility. Ploughing up of arable land leads to the loss of N in the form of mineralisation of organic N and the N release would follow the same trend as loss of C from soils (Behera and Sharma 2011; Barraclough et al. 2015). The large losses of soil organic C lead to a decrease in soil C storage (Melero et al. 2009). Therefore, the human factor (ploughing) changed the distribution of C and N content in arable land use, which may cause the C/N ratio in source areas to be lower than sink areas under arable land use. Conversely, this chapter could not find the exact cultivation history of all the grassland sites considered (e.g. when were they last ploughed or what land rotation scheme each was in). In addition, the fact that C/N ratio was lower in topsoil than subsoil under arable land use could be explained by leaching of soluble high C/N organic compounds. Diekow et al. (2005) showed that the C/N ratio increased with depth and explained that this trend might be due to soluble high

C/N soluble organic compounds leaching into deeper soil. The trend of C/N ratio increasing with depth was in line with the results of arable land use had a higher C/N ratio in subsoil than topsoil in this chapter. In arable land use, the high C/N soluble organic compound from crop residue would leach deeper into the soil and lead the C/N ratio in the subsoil to be higher than the topsoil. Another potential explanation is that some of the data sets on denitrification and BNF collected from publications used to calculate the N budget were outdated. This could have led the N budget (sink or source status) to be wrong, especially for arable land.

Human activities have produced excessive anthropogenic Nr that comprise all N species other than $N_2$ and, therefore, it was the dominant reason for changing the circulation of N through Earth's atmosphere, hydrosphere, and biosphere (Galloway et al. 1996). The Trent catchment has a large agricultural region where the anthropogenic Nr input is very high compared to other N inputs. Total anthropogenic Nr input to Trent catchment was estimated to be 13.5 tonnes N/km$^2$/yr, which is higher than other regions of a similar area (Table 3.5). This is due to its relatively high population, high livestock density and a high proportion of arable land (Table 3.5). Because the overall N use for crops and grass was obtained from the British Survey of Fertilizer Practice (2015), the crop areas were assumed to have the same fertilizer application rate across GB. The Trent catchment has a high proportion of arable land which led received a large amount of the fertilizer application input, moreover, the fertilizer input was the largest N input, thus the anthropogenic Nr input in the Trent catchment is larger than other catchments of a similar area. However, the flux of total N input in the Thames catchment in 2015 was estimated to be 17.4 tonnes

N /km$^2$/yr, which is higher than the Trent catchment. Although the proportion of arable in the Thames catchment is lower than the Trent catchment, the population of Thames catchment is much higher than Trent catchment. The food and feed transfer for the Thames catchment was greater than for the Trent catchment. Thus, the total N input to the Thames catchment was higher than for the Trent catchment. Furthermore, both Thames and Trent catchments had a high proportion of arable land use with high fertilizer application rates than other catchments. The high fertilizer application could result in high N gas emission, and most of the N gas would be deposited to the terrestrial biosphere. Therefore, the flux of N deposition in the Trent and Thames catchment was probably higher than other catchments.

**Table 3.5:** Comparison of N inputs to the Trent catchment with other regions of similar area.

| District | Area (km$^2$) | Arable area (% of catchment) | Total N input per unit area (tonnes N/km$^2$) |
|---|---|---|---|
| Kennebel | 13994 | 6 | 1.1 |
| Merrimack | 12005 | 8 | 2.2 |
| Hudson | 11942 | 10 | 2.0 |
| Androscoggin | 8451 | 5 | 1.3 |
| Mohawk | 8935 | 28 | 3.6 |
| Trent | 8231 | 46 | 13.5 |

The predicted atmospheric N emission dominated the N output, accounting for 55% of total N output in the Trent catchment. Skiba et al. (2012) claimed that

fertilizer was the largest source of agricultural N emissions. The high atmospheric N emissions were caused by fertilizer application, manures, urine deposition and crop residues. In the Trent catchment, the average value of atmospheric N emission export was 4.4 tonnes N/km$^2$/yr which is higher than the average value for the UK of 2.3 tonnes N/km$^2$/yr (Worrall et al. 2016a). The relationship between atmospheric N emission and N deposition has been calculated by many studies (Asman 1998; Goulding et al. 1998; Kanakidou et al. 2016). More atmospheric N emissions lead to more N deposition. Tonnesen et al. (2003) have claimed that high N deposition rates may take place in areas of downwind of agricultural sources. The Trent catchment had higher predicted atmospheric N emission than reported for other catchments such as the Thames (National Atmospheric Emissions Inventory 2015). However, the N deposition in the Trent catchment was less than that estimated for the Thames catchment and even predicted was lower than the average value of the UK. This is because previous studies only considered the relationship between total N deposition and total N emission rather than considered the spatial distribution. That said, the relationship between total N deposition and total N emission cannot prove that high atmospheric N areas had a high N deposition rate. Because the atmospheric N gas can be transported by wind, high N deposition may not take place near sources of N emission.

The United States Department of Agriculture (2011) reported that C/N ratios around 25 were considered optimal for microbial activity. Lower C/N (less than 25) ratios would decrease N immobilization potential, which increases the soil $NO_3^-$ concentration and may result in high N loss rates and low C sequestration rates.

The average C/N ratio of the sink areas was lower than the source areas, which supports the view that N stores were larger in sink areas than in source areas. Cleveland and Liptzin (2007) reported that the C/N stoichiometry in soil remains stable at 14 on the global scale. In the UK, Henrys (2012) showed that the C/N ratios under arable land use varied between 9.37 and 17.22, with an average of 11.42 and the C/N ratio under grassland use varied between 9.81 and 29.03, with an average of 15.32 (Table 3.6). Although the C/N ratio under arable land or grassland in this chapter showed similarities to the Henrys (2012) findings, this study's C/N ratio under grassland was lower than the C/N ratio in Henrys (2012). However, this study's C/N ratio under arable land was higher than the C/N ratio in Henrys (2012). Moreover, the application of too much N fertilizer and high N content of crop residue input may narrow the C/N ratio. Therefore, the low C/N can be considered as a necessary condition for N accumulation.

**Table 3.6:** The C/N ratio of different land use across the UK.

| Land use / C/N ratio | Arable land use | Grass land use |
|---|---|---|
| Minimum | 9.37 | 9.81 |
| Maximum | 17.22 | 29.03 |
| Mean | 11.42 | 15.32 |
| Mean this study | 13.22 | 11.54 |

## 3.5 Conclusions

This chapter considered the spatial N budget across the Trent catchment for 2015, where 69% of grid squares were predicted to be sink areas and 31% were source areas. In 2015, the Total N budget showed that the Trent catchment has been accumulating total N. The accumulation of total N in the catchment was estimated to be 35 ($\pm$5) ktonnes N in 2015.

The hypothesis in this chapter was that N accumulation occurs in the subsoil of the Trent catchment and C/N ratio was used to test this hypothesis. The expected result was that the depth profile would have a significant effect upon the C/N ratio between sink areas and source areas, but only a part of this was found to be the case. The subsoil C/N ratio in sink areas was found to be significantly lower than the C/N ratio in the subsoil of areas identified as being of net total N loss under grassland but not for arable land. Overall, this indicates that accumulation of N could be occurring in subsoils under grassland but not under arable land.

# Chapter 4

# Temporal Variability in the Trent catchment N budget

## 4.1 Introduction

A number of time series studies have already considered the N budget (Bashkin et al. 2002; Ti et al. 2012; Worrall et al. 2016a). These studies do not only estimate the N change over time but also enable forward projection to project N budget change in the future. An N budget trend can help understand what factors control each N flux in the future and so manage N-related environmental degradation (Oenema et al. 2003). An N budget includes many different N flows and some of there that have response times of many years. Mineralization and immobilization result from land use change may have response time, especially for groundwater dominated catchments as solute travel time may be many decades. Addiscott (1988) and Whitmore et al. (1992b) showed that the response time of net soil N mineralization and immobilization to land use change can be decades. Land use change also may

perturb the aquifer system. When an aquifer system is perturbed, it will take from just a few seconds to possibly millions of years evolve to a new equilibrium. Thus, groundwater response times to land use change can be decades (Howden et al. 2011b; Sophocleous 2014). In addition, land use change can disturb the state of equilibrium of soil N storage. This can take several decades to reach a new state of equilibrium (Knops and Tilman 2000). Therefore, in the context of continuing N pollution, a temporally-resolved N budget could help understand N cycling through the environment. Previous time series studies have focus on N the budget for a particular region. However, no previous study has considered the spatial heterogeneity of an N budget with time (Worrall et al. 2009; Howden et al. 2011a). This chapter aims to estimate the temporal variability in the spatial N budget of the Trent Catchment.

Recent studies (Bell et al. 2011; Barraclough et al. 2015) observed that N released from soils follows the same trend as C loss from soils. Thus, land use change may exert a similar effect on soil N storage as on soil C (Leifeld 2013). Many studies have focused on particular ecosystems, including forest ecosystems (Goodale et al. 2002); grass ecosystems (Ammann et al. 2009) and crop ecosystems (Bassanino et al. 2007). However, due to their interconnectedness, N circulates through and between these ecosystems. Thus it is important to understand how N cycles through entire catchments including different ecosystems. Additionally, while fertilizer application rates have decreased yearly since 1990 (British Survey of Fertilizer practice, 1992~2015), total N fluvial flux from the land surface has not followed the same trend (Worrall et al. 2012a). This contrast suggested that diffuse source N pollution from fertilizer can take a long time to adjust to changes in inputs. The time

required is likely to vary with land use and soil type (Makoto et al. 2005). While a spatially-differentiated N budget for the Trent catchment was presented in chapter 3, this chapter aims to elucidate how the spatial N budget for the Trent catchment has varied with time and will continue to do so in the future. In addition, this chapter aims to understand: i) how N budgets vary according to land use within the Trent catchment; ii) how the spatial distribution of N sink and source areas varied from 1990 to 2015; and iii) how land use changes may have impacted the storage and release of N.

## 4.2 Methodology

The model described in this chapter includes all significant N terrestrial input and output pathways over a period of time. It was possible to calculate all the fluxes for a spatially-differentiated total N budget between 1990 and 2015. The estimates were possible for all individual N pathways and where that was the values for that N pathways are reported from 1990 to 2015. For all N input and output pathways that could be included, the resulting time series from 1990 to 2015 were also projected forward to the future using linear extrapolation. Linear extrapolation may be overly simplistic, thus, factors responsible for recent trends can be used alongside simple linear extrapolation to predict the total N budget in the future. However, when looking the trend from 1990, the caveats that the 1990 data is not compatible with the later data was considered in this chapter. In this chapter, the convention used is the same as in previous chapters that a negative budget is a source of N and positive value is a sink N budget.

The N input and output pathways considered in the present chapter are the same as in Chapter 3. The methodology for calculating all the fluxes for a total N budget between 1990 and 2015 was as described in Chapter 3. The uncertainty of each N input and output pathway was considered for each 1 $km^2$ grid of Trent catchment was the same as the uncertainty of each N pathway in chapter 2. A total of 1000 Monte Carlo simulations were used to quantify the overall uncertainty for total N budget. Land use as a key component of the N budget was collected from Digimap for the years 1990, 2000, 2007 and 2015 (CEH:www.ceh.ac.uk) for 1990-2015. The total N budget for any year was calculated as the sum of all N inputs and outputs (same as chapter 2). The N budget time series for the Trent catchment calculated herein, provides critical information concerning how land use changes affect the release of N in terrestrial biosphere.

To forecast future changes in the spatial total N budget for the Trent catchment, the spatial N budgets for 1990, 2000, 2007 and 2015 were used to understand the historical trend and try to forecast the future trend. In addition, most N flux excluding N deposition, N atmospheric emission, human consumption and net livestock input are related to land use, population density or livestock numbers, and so the time courses of these drivers were used as predictors to estimate future trends. Population and urban land use can be expected to increase in the future, although population growth rates are expected to decrease with time (https://www.ons.gov.uk). Therefore, the trend of each N flux related to these factors (land use, population and livestock number) was projected into the future. This chapter presents two scenarios based on urban land use and population, both factors expected to increase in the

future, to predict GB's future N budget. Scenario 1 describes how the N budget will change in the future as population increases (not consider other factors), and, scenario 2 describes how the N budget will change as urban land use expands in the future (not consider other factors and land uses).

## 4.3 Results

### 4.3.1 Time series of N budget

#### Temporal change in drivers of N flux

Land use was summarised as arable land use, grass land use, urban land use and other land use (Figure 4.1). In the Trent catchment, arable land use decreased from 4,987 $km^2$ in 1990 to 3,751 $km^2$ in 2000. Then arable land use increased to 4,283 $km^2$ in 2007 followed by a decrease to 3,687 $km^2$ by 2015. Grass land use increased from 3,482 $km^2$ in 1990 to 4,030 $km^2$ in 2000. Then grass land use decreased to 3,774 $km^2$ in 2007 followed by an increase to 3,942 $km^2$ in 2015. Urban land use more than doubled from 210 $km^2$ in 1990 to 471 $km^2$ in 2015. Livestock numbers and population are summarised in Figure 4.2. The population for the Trent catchment, as derived from Census returns, increased 5,967,835 from 1990 to 6,357,699 in 2015. The sheep number increased from 1,023,686 to 1,137,710 between 1990 and 2000 but fell to 899,833 in 2015. The cattle number decreased from 656,058 in 1990 to 584,736 in 2015. Pig number increased from 341,350 in 1990 to 378,544 in 2015 but fell to 266,136 in 2015. Poultry number decreased from 11,469,918 to 11,092,904 during 2000 and 2015 followed by an increase from 8,875,303 in 1990 to 11,469,918

in 2000.

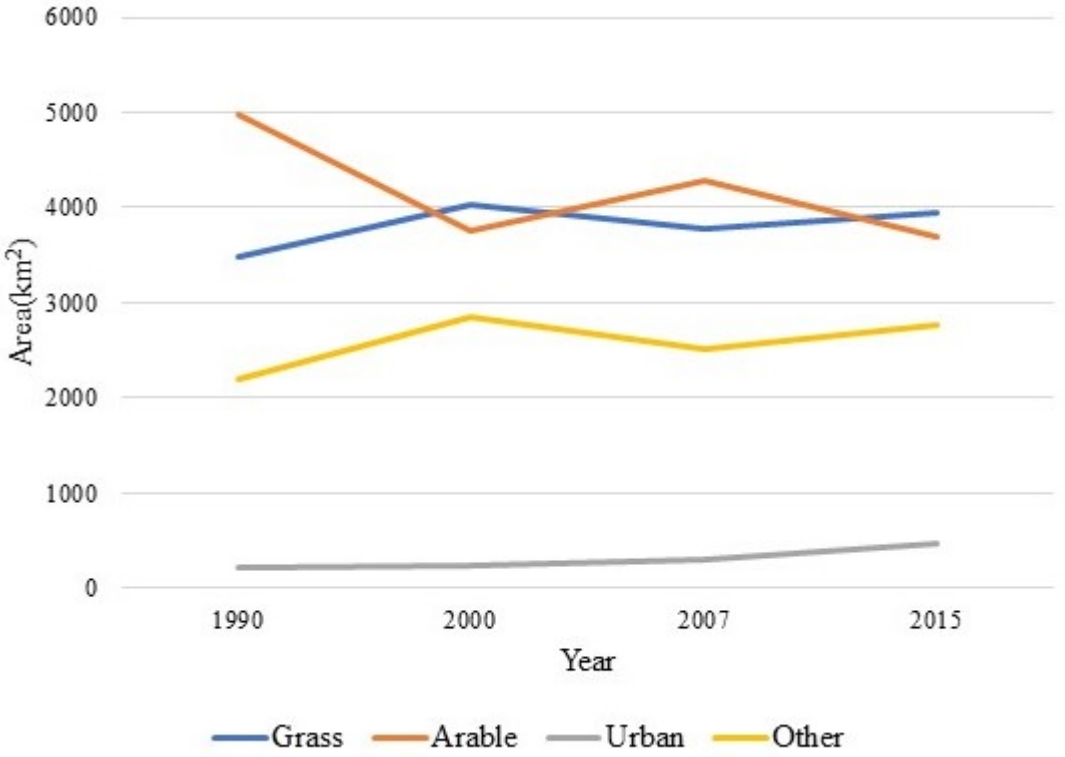


**Figure 4.1:** Summary of land use for Trent catchment between 1990 – 2015 ($km^2$).

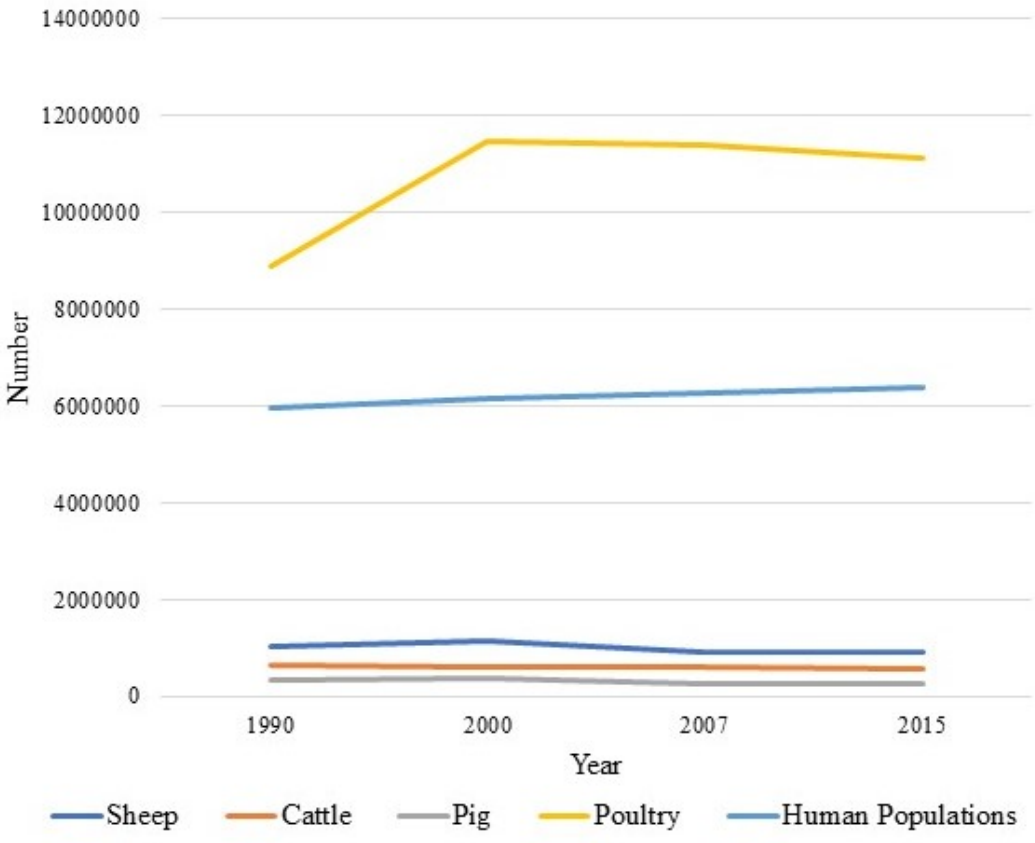


**Figure 4.2:** Summary of livestock number and population for Trent catchment between 1990-2015.

### Temporal changes in N inputs

Table 4.1 provides the summary statistics for total N inputs, outputs and changes over the study period. In the Trent catchment, chemical fertilizer represented the highest N input in all years. However, this decreased by 28% from 105 $\times 10^3$ tonnes N in 1990 to 76 $\times 10^3$ tonnes N in 2015 (Figure 4.3), the estimated error on the fertilizer is $\pm 9\%$. In GB, the data for fertilizer application rates have been collected back to 1990 and fertilizer application rates decreased, thereafter, partly as an effort to reduce greenhouse gas emissions and partly in response to restrictions in N use in

Nitrate Vulnerable Zones (British Survey of Fertiliser Practise 2017). The long-term decline in total N fertilizer use over this period was derived by a decrease in average fertilizer application rate. Because the average value of fertilizer input of arable land use is larger than that for grass, areas of arable land use converted to grassland resulted in a decrease in the N fertilizer input over the study period.

**Table 4.1:** Predicted changes of nitrogen input, output, and budget between 1990 and 2015 in the Trent catchment ($10^3$ tonnes N/yr).

| | 1990 | 2000 | 2007 | 2015 |
|---|---|---|---|---|
| Fertilizer N | 105 | 95 | 88 | 76 |
| Biological N fixation | 12 | 20 | 18 | 19 |
| Atmospheric deposition | 17 | 18 | 16 | 16 |
| Human N consumption | 27 | 28 | 29 | 31 |
| Net livestock N input | 13 | 14 | 12 | 12 |
| Total input | 174 | 174 | 164 | 154 |
| Atmospheric N emission | 125 | 83 | 69 | 47 |
| Denitrification | 10 | 9 | 9 | 9 |
| Total fluvial N flux | 35 | 24 | 22 | 28 |
| Groundwater N loss | 0.5 | 0.5 | 0.5 | 0.5 |
| Crop N removed | 47 | 36 | 41 | 35 |
| Total N output | 217 | 152 | 142 | 119 |
| Total N budget | -43 | 22 | 23 | 35 |

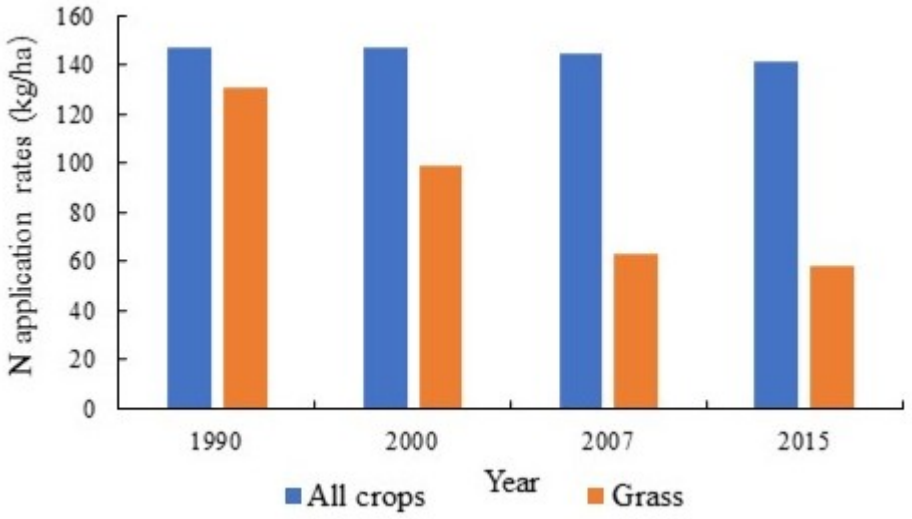


**Figure 4.3:** N fertilizer applications in Trent catchment on arable land and grassland between 1990 and 2015.

BNF increased from 12 $\times 10^3$ tonnes N in 1990 to 19 $\times 10^3$ tonnes N in 2015. However, from 2000 to 2007, the BNF decreased from 20 $\times 10^3$ tonnes N to 18 $\times 10^3$ tonnes N as areas of N-fixing crop decreased. The estimated error on the BNF is $\pm$ 25%. Because BNF was assumed to be directly correlated with land use, the observed changes in the predicted BNF time series are driven by land use change. The N deposition was independently calculated over the study period. In the Trent catchment, N deposition decreased from 17 $\times 10^3$ tonnes N in 1990 to 16 $\times 10^3$ tonnes N in 2015. Because most of the Trent catchment is agricultural land, the source of N deposition most likely came from agricultural production resulting in emission of N gases (i.e. N gas from fertilizer). In addition, European N gas emissions have decreased since 1990 due to effective environmental protocols and economic restrictions (Metcalfe et al. 1999). Most N gas emissions from the terrestrial biosphere are deposited as wet and dry deposition (Fenn et al. 2003). Therefore, the N depo-

sition decreased following the decreasing trend of N gas emission. However, the N deposition was 18 $\times 10^3$ tonnes N in 2000, which is the largest over the study period.

Although human N consumption was not assumed to be directly correlated with land use, it is correlated with the population. The human N consumption was driven by population, increased over the study period. Human N consumption was calculated to increase by 0.5% per year over the period of study from 27 $\times 10^3$ tonnes N in 1990 to 31 $\times 10^3$ tonnes N in 2015. The error estimate from human consumption was taken as the default of $\pm$ 80%. Livestock N input was assumed to be correlated with livestock numbers (cattle, sheep, pig and poultry). There was a change in the number of each type of livestock in the catchment over the study period, Table **??**, which resulted in a small N input change from 13 $\times 10^3$ tonnes N in 1990 to 14 $\times 10^3$ tonnes N then remained stable at 12 $\times 10^3$ tonnes from 2007 to 2015.

### Temporal change in N outputs

Total N atmospheric emissions represented the highest predicted N output in the Trent catchment. This decreased from 125 $\times 10^3$ tonnes N in 1990 to 47 $\times 10^3$ tonnes N in 2015, a decrease of 4% per year. The estimated error on the total N atmospheric emission is $\pm$ 80%. Total N atmospheric emission was independent of land use change across the Trent catchment. The atmospheric emission decreasing may be caused by emission reduction strategy implement in Trent catchment. In the present study, the highest concentrations of N gas were observed in N gas source areas (i.e. agricultural areas). The N emission occurred in agricultural land use areas in Trent catchment.

The total fluvial N flux was estimated by multiple regression model from chapter

3, which decreased from 35 $\times 10^3$ tonnes N to 22 $\times 10^3$ tonnes N between 1990 and 2007, while from 2007 to 2015, the fluvial N flux increased from 22 $\times 10^3$ tonnes N to 28 $\times 10^3$ tonnes N (Table 4.1). The estimated error on the fluvial flux calculation is $\pm$ 32%. From Table 4.1, the proportion of N fluvial flux in the total N input was 13% - 20%. The proportion of total N fluvial flux was similar to estimate from Howarth's result (Howarth et al. 1996) of 10% - 25% in 14 regions in North America.

Crop N removed (Table 4.1) was assumed to be related directly with arable land use in this study. No crop N was assumed to be removed for non-arable land use. The crop removed changed with the arable land use over the study period. Specifically, crop removed decreased from 47 $\times 10^3$ tonnes N in 1990 to 36 $\times 10^3$ tonnes N in 2000 and increased to 41 $\times 10^3$ tonnes N in 2007 followed by a decrease to 35 $\times 10^3$ tonnes N in 2015.The error on this crop N removed is $\pm$ 80%.

Because fixed denitrification rates were assumed for each land use investigated in this study, any temporal trends in denitrification are the result of land use changes only. Total denitrification was predicted to decrease from 10 $\times 10^3$ tonnes N in 1990 to 8 $\times 10^3$ tonnes N in 2015. The error on this denitrification is $\pm$ 96%.

### Temporal change of total N budget

Predicted total N input, including N deposition, BNF, N fertilizer application, net livestock N input and human N consumption, decreased by 0.5% per year from 174 $\pm$ 15 $\times 10^3$ tonnes N in 1990 to 154 $\pm$ 13 $\times 10^3$ tonnes N in 2015. Total N outputs, including N emission, total N fluvial loss, denitrification, crop N removed and groundwater N loss, decreased by 0.2% per year from 217 $\pm$ 21 $\times 10^3$ tonnes N in 1990 to 119 $\pm$ 9 $\times 10^3$ tonnes N in 2015. The largest contributor to the decrease

in N input was a decrease in fertilizer N inputs, which accounted for 57% of total N input changes over the study period. The largest contributor to the decrease in N output was decreasing atmospheric N emission, which accounted for 79% of total N output change over the study period. The N budget changed from a net source of -43±7 $\times 10^3$ tonnes N in 1990 to a net sink of 35±5 $\times 10^3$ tonnes N in 2015 (where the value given is the mean ± standard error). This is because predicted total N output declined faster than predicted total N input.

### 4.3.2 Spatial change of N inputs and outputs during the study period

In this chapter the spatial change for the different N inputs and outputs were estimated over the period from 1990 to 2015 (Figure 4.4, 4.5 and 4.6). A large change of in fertilizer input was predicted in the mid-north of the Trent catchment, which was caused by a change in both fertilizer application rate and the proportion of arable land use in each grid cell over the study period (Figure 4.4a). In each year, the spatial distribution of N fertilizer input was the same as the distribution of grass and crop. Thus, the highest N fertilizer input is observed in the east and mid-north of the catchment (Figure 4.4a). Major N fixing crops and grassland were primarily located to the north-west of the Trent catchment. These areas exhibited the highest BNF inputs compared to other areas (urban land use and non-fixing crops areas). Areas with the greatest BNF change were located in the north-west and mid-north of the Trent catchment, mainly caused by the expansion of N fixing crops (Figure 4.4b). N deposition was not assumed to occur close to N gas emissions

due to atmospheric mixing. Most areas (96% of total Trent catchment) showed a decrease in the magnitude of N deposition during the study period. Areas for which was an increase in N deposition assumed were mainly located in the north-east and north-west of the catchment (Figure 4.4c).

Human consumption of N (input per $km^2$) is assumed to be proportional to population density. This increased as the average number of individuals per unit of area increased during over study period. The greatest change in human N consumption was thus observed in urban areas (i.e. Birmingham, Leicester, Derby and Nottingham) where the population in urban areas was higher than other regions (Figure 4.5a). Assuming that the rate of population growth was the same for all regions and the number of people in urban areas was higher than that of other regions, then the change of population in urban area was higher than other regions. Therefore, the change of human N consumption in urban areas was higher than in other regions.

Livestock input was assumed to be proportional to livestock numbers. Livestock numbers decreased over the study period, which meant all agricultural areas of the Trent catchment showed a decrease. The highest change in livestock input was mainly located in the mid-east, mid-west and north-west of the Trent catchment (Figure 4.5b).

Total atmospheric N emissions was an independent pathway which has no relationship with land use or population change. The N emission pathway showed a decrease in all areas over time. The greatest N emission changes were mainly in the mid-west and east of the catchment (Figure 4.5c).

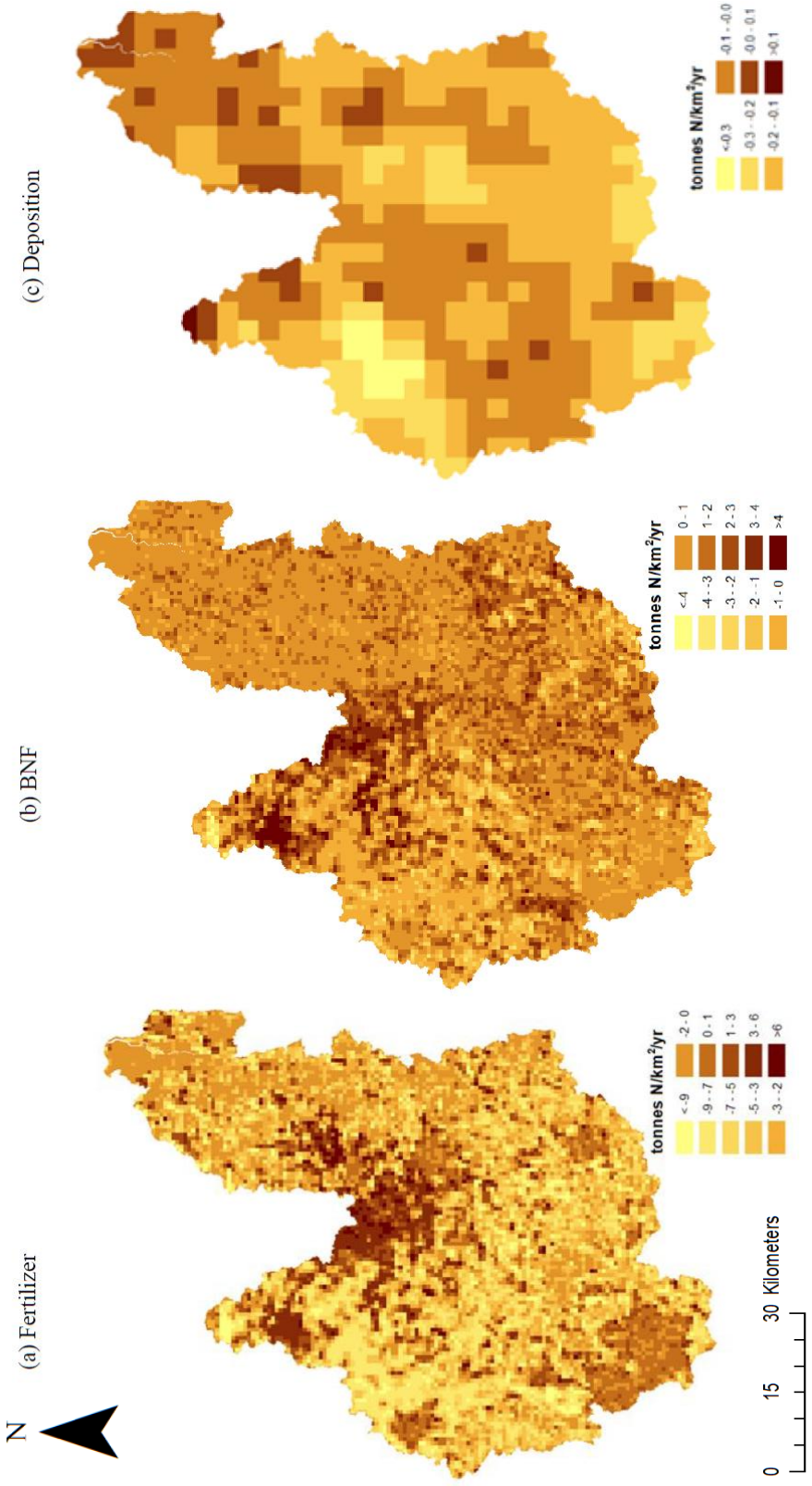


**Figure 4.4:** Spatial patterns of the change in fertilizer application, BNF and N deposition in the Trent catchment from 1990 to 2015.

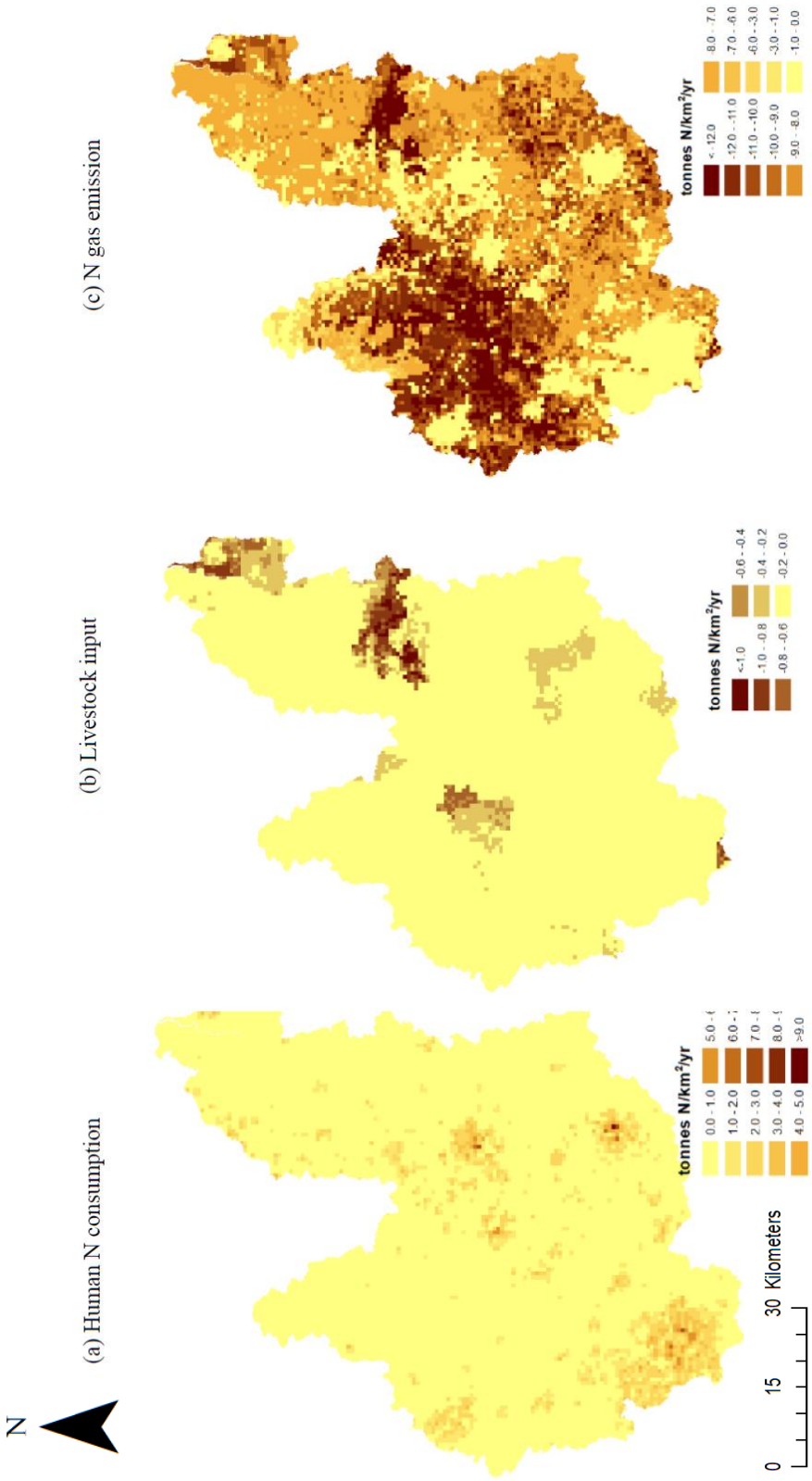


**Figure 4.5:** Spatial patterns of the change in Human N consumption, livestock N input and N gas emission in the Trent catchment from 1990 to 2015.

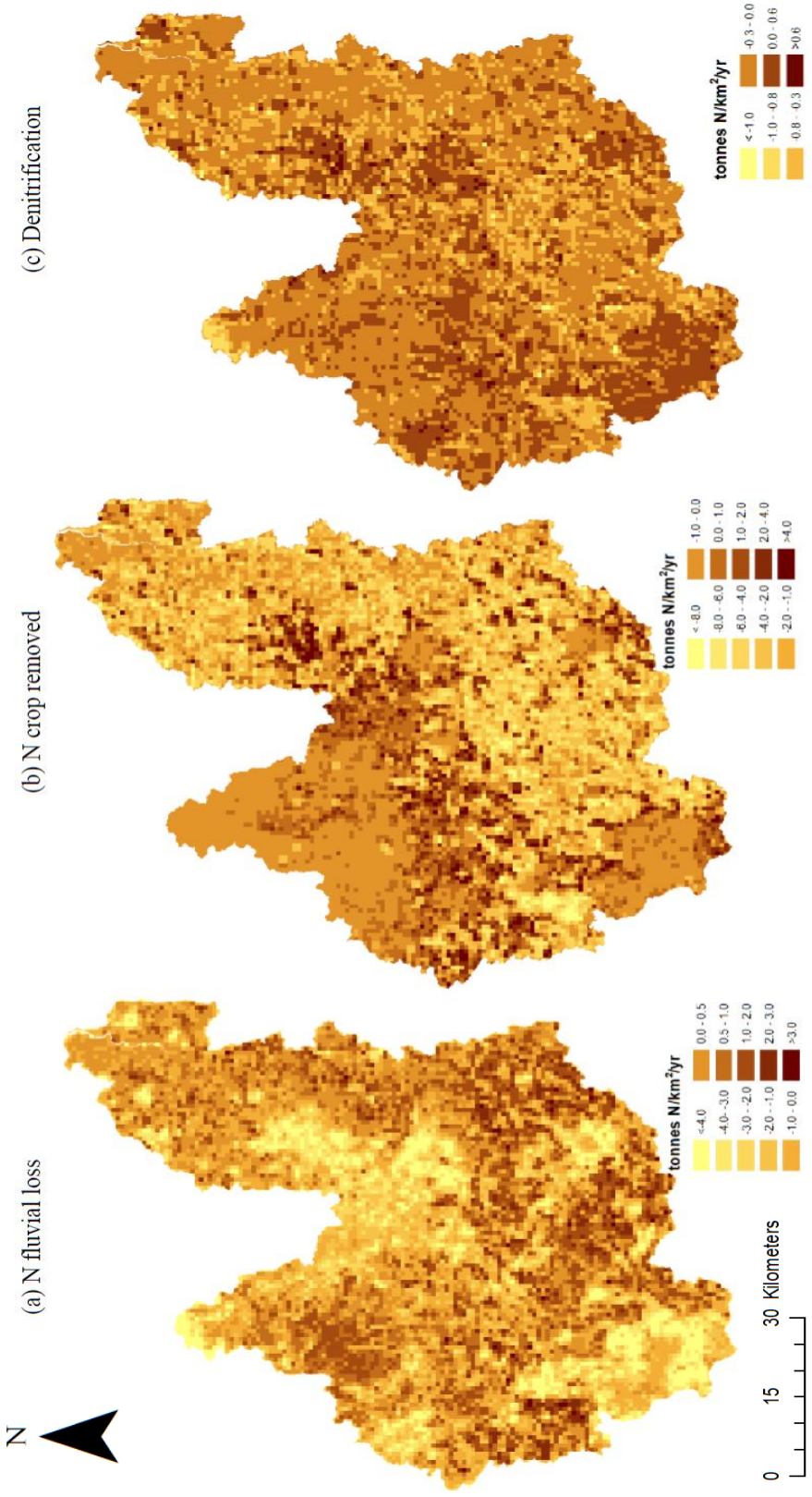


**Figure 4.6:** Spatial patterns of the change in N fluvial loss, N crop removed and Deposition in the Trent catchment from 1990 to 2015.

46% of the Trent catchment showed an increase in N fluvial loss which occurred mainly in the east and north-west parts of the catchment (Figure 4.6a). The remainder (54%) showed a decrease in the total N fluvial flux, primarily in the central, south-west and southeast sectors of the Trent catchment where urban land use dominated (Figure 4.6a).

The spatial pattern of change in crop N removal over time resembled that of arable land use change. The increase in crop N removal mainly occurred in the mid-west of the catchment, caused by an increase in arable land use in this area (Figure 4.6b). The north-west and east of the catchment showed a decrease in crop N removal during the study period (Figure 4.6b).

Change over time in denitrification N output correlated with land use change - 27% of areas in the Trent catchment showed an increase in the magnitude of denitrification, mainly in urban areas (e.g. close to Birmingham, Nottingham, Derby, Stoke and Leicester). The remainder (73%) of the Trent catchment was show predicted to a decrease in the magnitude of denitrification - primarily in agricultural areas located in the east and mid-south of the Trent catchment (Figure 4.6c).

### 4.3.3 Spatial N budget change and statistics from a land use perspective

The estimate of the overall budget suggests that total N was a net source flux of -43±7 $\times 10^3$ tonnes N/yr in 1990 (where variation is quoted as the standard error) changing to a net sink in 2015 at 35±5 $\times 10^3$ tonnes N/yr. The spatial total N budget varied with time across the Trent catchment (Figure 4.7). Specifically, the

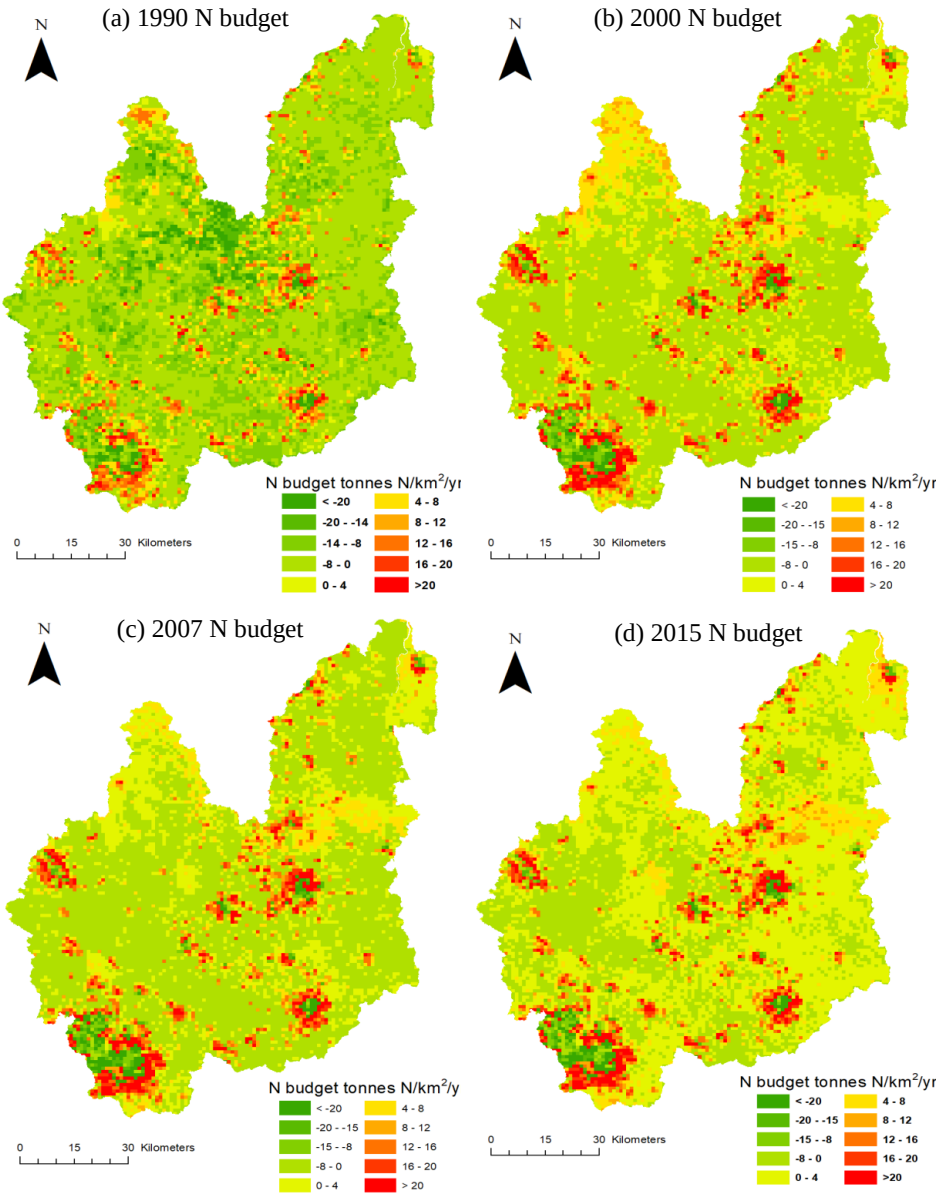


**Figure 4.7:** Spatial distribution of the Total N Budget for the Trent catchment according to year.

proportion of sink areas in the Trent catchment increased from 23% in 1990 to 43% in 2000. Then, the proportion of sink areas in the Trent catchment decreased from 43% in 2000 to 42% in 2005, followed by an increase to 69% in 2015 (Figure 4.8). Conversely, the proportion of source areas decreased from 77% in 1990 to 57% in 2000. Then, the proportion of source areas in the Trent catchment increased from

57% in 2000 to 58% in 2007 followed by a decrease to 31% in 2015 (Figure 4.8).

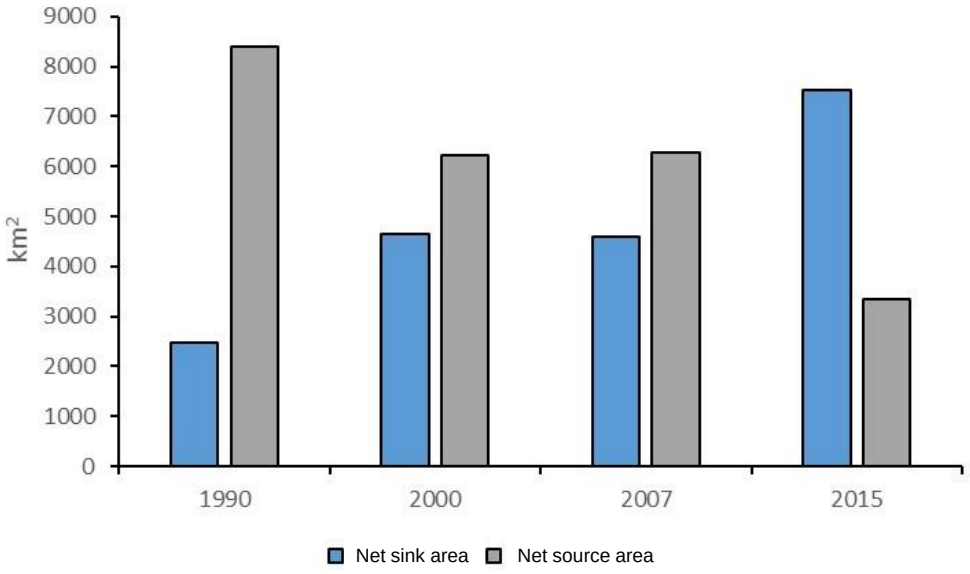


**Figure 4.8:** The proportion of sink and source areas in Trent catchment according to year.

The distribution of high N output regions was consistent with high N input regions. Between 1990 and 2015, the total N budget of the Trent catchment transitioned from source to sink. In 1990, 77% of the Trent catchment area (primarily in the east and mid-west of Trent catchment) were source areas. The proportion of source areas in the catchment decreased from 77% in 1990 to 31% in 2015 (Figure 4.8). Because most N pathways are directly related to land use, variations in the total N budget through time are largely associated with changes in land use. Maps of land use change in the Trent catchment, for 2000, 2007 and 2015 respectively, are given in Figure 4.9. Figure 4.10 shows a map of the change of total N budget caused by land use during this period with six types of N budget change identified. Specifically, red areas denote a decrease in the magnitude of net source N budget. Green areas denote an increase in the magnitude of net source N budget. Yellow

areas denote a decrease in the magnitude of sink N budget. Black areas denote an increase in the magnitude of sink N budget. In addition, the transition between a sink N budget and a source N budget are also shown in Figure 4.10. Blue areas show the sink areas transferred to source areas. Violet areas show the source areas which transferred to sink areas. Figure 4.10 shows the effect of land use changes over 1990 – 2015, and the magnitude of total N budget change with land use change. Specifically, 65% of the areas in the Trent catchment showed a predicted decrease in the magnitude of net source N budget, mainly in the north-west, north and east of the Trent catchment (Figure 4.10d). In addition, 17% of areas in the Trent catchment showed a decrease in the magnitude of total N sink, concentrated near cities mainly caused by urbanisation (grass change to urban and arable change to urban). While, 18% of areas in the Trent catchment showed a decrease in the magnitude of source N budget, an increase in the magnitude of sink N budget and a transferred status of N budget (sink changed to source and source changed to sink). Urban land use centres did not change during this period, but the magnitude of s N budget still showed a decrease. Grassland, especially in the mid-west, was transformed to arable, which caused a decrease in the magnitude of the N sink budget. Therefore, decreased urban land use and arable land use may transfer the total N budget from source to sink. Urban land use increased from 210 $km^2$ in 1990 to 472 $km^2$ in 2015, but the proportion of urban area was lower than other land uses (arable, grass and other) (Figure 4.11). Arable land use had the largest predicted decrease in land use over the study period (i.e. 1990 to 2015), with 1,300 $km^2$ changed from arable to other land uses (urban, grass and other) (Figure 4.11). Therefore, arable land use

change was the main reason for changing net source N flux from -43±7 $\times 10^3$ tonnes N in 1990 to net sink in 2015 at 35±5 $\times 10^3$ tonnes N.

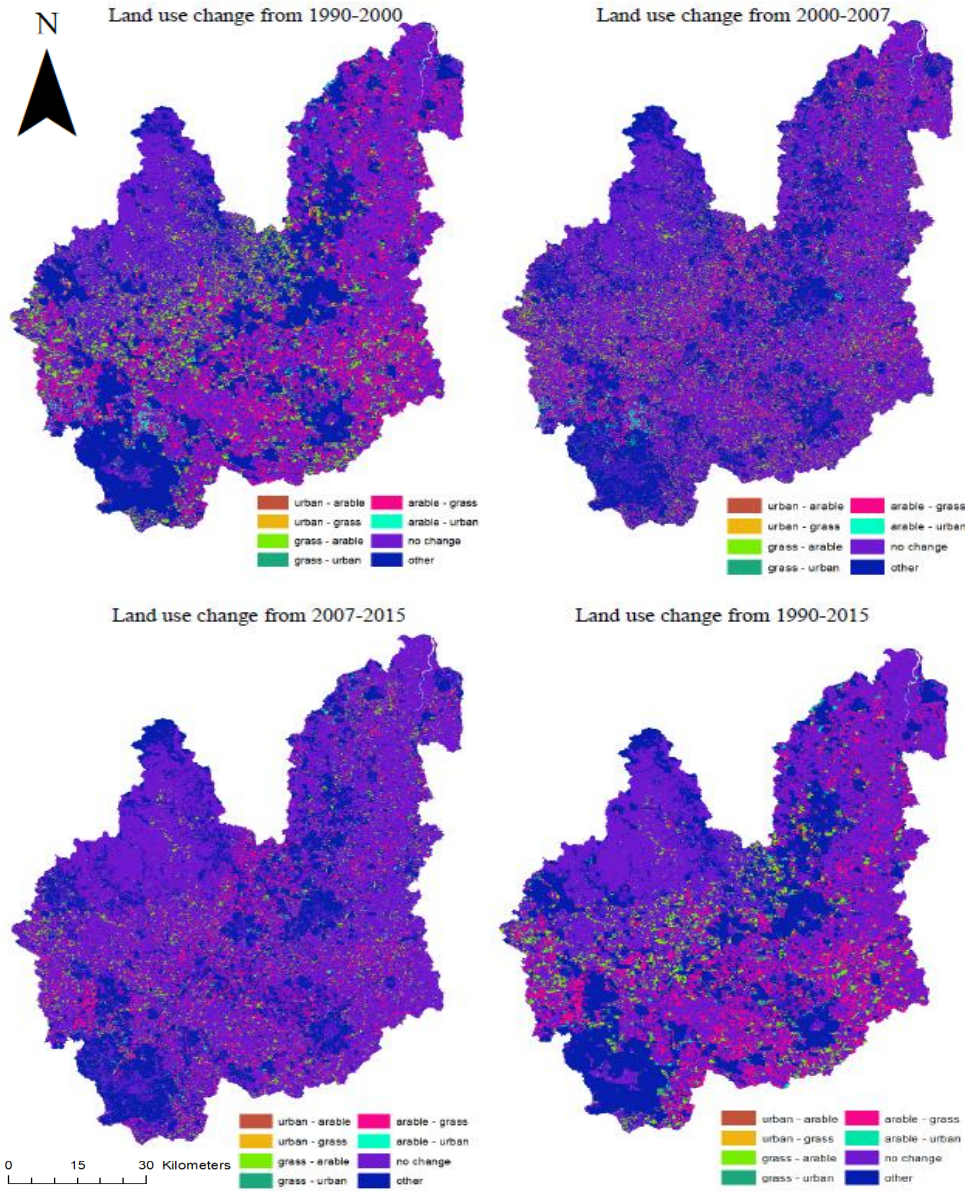


**Figure 4.9:** Land use change over 1990 - 2015.

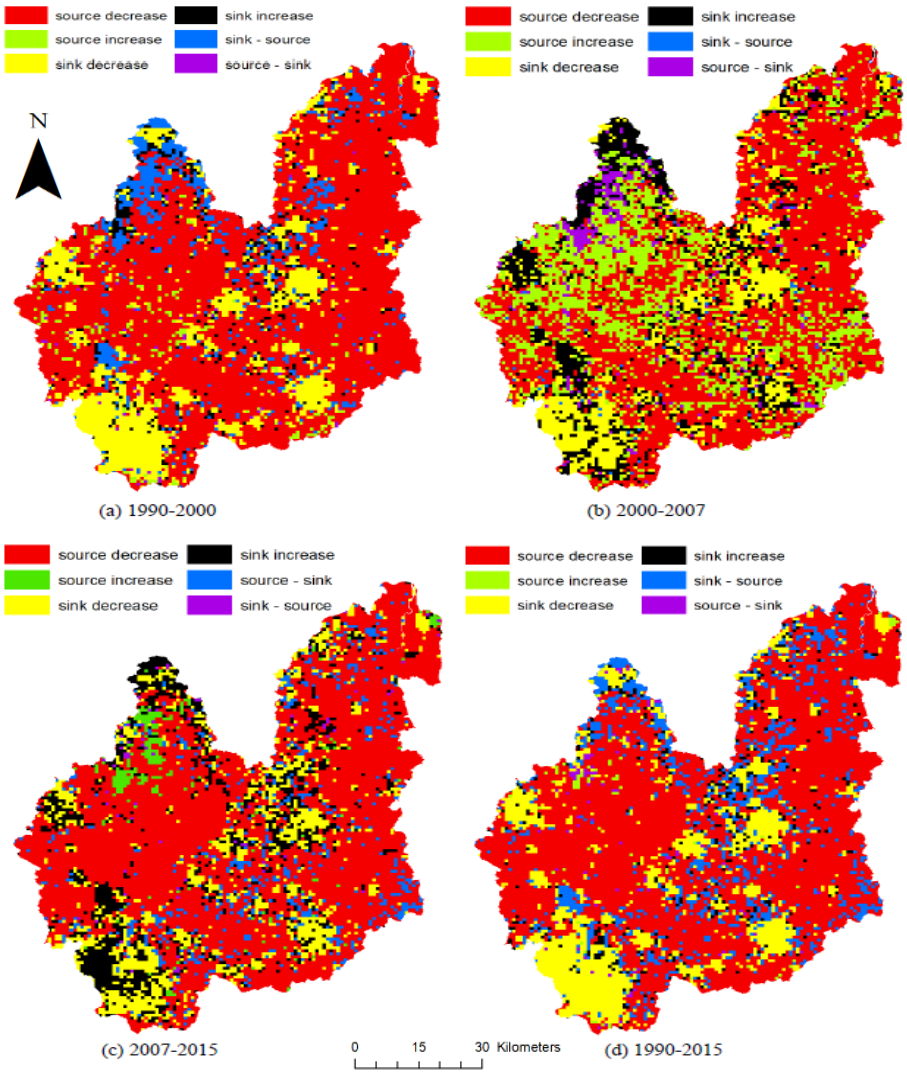


**Figure 4.10:** Spatial distribution of the direction of change in the Total N Budget according to year.

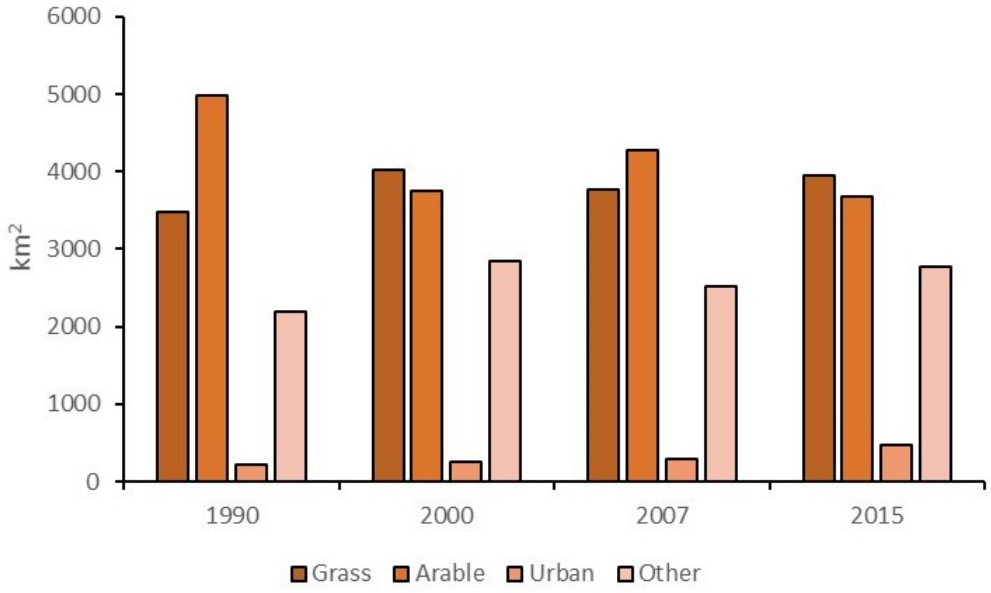


**Figure 4.11:** Land use change for the years of study between 1990 and 2015.

The estimate of the total N budget in this chapter suggested that the Trent catchment total N was a net source flux of -43 ($\pm$7) $\times 10^3$ tonnes N in 1990 changing to a net sink flux of 35 ($\pm$5) $\times 10^3$ tonnes N in 2015. Based on simple linear extrapolation, this chapter showed that since 2000 the Trent catchment has been accumulating N and that the magnitude of the sink N budget is likely to continue in the future.

This study also considered scenarios of future change in the N budget based on trends in urban land use and population alone (no information about how other factors change in the future). Over the period 1990 – 2005, total human consumption input was proportional to population density; per-capital N flux was 5 $\times 10^{-3}$ N/yr. According to Scenario 1, with an increasing population, the Trent catchment would increase the value of N accumulation. With respect to the spatial N budget across the Trent catchment, the N budget of each grid would change as people move in/out

of each area. Although urban land use increase directly relates to decreasing total N budget, expanding urban land use will make other land uses shrink, which also impacts the total N budget. Because there is no detailed information about how much urban land will change in the future and which land use will change to urban land use, it is impossible to calculate how much will be expected per $km^2$ land use change. The relationship between N pathway and urban land use showed that an increase in urban land use would decrease N input and increase N output. Therefore, according to Scenario 2, in a future where urban land use increases but other factors remain the same, the Trent catchment is likely to change from an N sink to an N source.

### 4.3.4 Discussion

Figure 4.7 demonstrates the spatial and temporal variation of the total N budget within the Trent catchment during the study period. Fertilizer was the largest N input, accounting for 49% - 51% of total N input. Fertilizer input also showed the greatest change, and hence it exerts a major over the total N budget trend and spatial patterns of change. Among all N pathways, thus, fertilizer input change would control the total N budget trend. Although changes in fertilizer input and total N budget over the study period differed, their spatial patterns were similar. The highest fertilizer input change and total N budget change both occurred in the north-central region of the Trent catchment (Figure 4.4a, Figure 4.10d). This is consistent with Galloway et al. (2008) who found that fertilizer input was the main control on N balance. The extent of crop area and fertilizer rates were two factors in

changing fertilizer input rate. The fertilizer input rate represents the overall fertilizer N application rate which was calculated by the total annual fertilizer use divided by arable areas and grass areas which means the fertilizer rate on arable and grass land use exhibits no variation across the Trent catchment. Therefore, fertilizer N input was controlled by the change of the proportion of land use in each 1 $km^2$. In addition, this chapter has shown that the total N budget of 2015 was the largest over the study period and the average value of total N budget of 2015 is 3.4 tonnes N / $km^2$ /yr - where the value was obtained from the total N budget was divided by total catchment area. To compare with N surplus intensity (defined as the difference between all N inputs and outputs per $km^2$), the average NSI value for England at 2015 was 5.1 tonnes N/$km^2$/yr (Defra (2015b)), higher than the value observed for the Trent catchment despite its importance as an agricultural region in England (the agricultural regions should have high NSI when considering all N inputs and outputs). The average NSI value for England was higher than the average N export value suggested that earlier estimated of NSI was not based on a complete N budget, and missed some N output pathways.

The total N deposition should show a decrease from 1990 to 2015 as the N emission decrease over the study period. However, N deposition in 2000 was higher than in 1990. This is maybe due to higher average annual rainfall in this year relative to the other years (`https://www.metoffice.gov.uk/`). More rainfall would bring more wet N deposition to land. Fowler et al. (2005) stated that the ratio of wet to dry N deposition was controlled by wet deposition, which accounted for the majority of total N deposition. Therefore, the total N deposition was higher in 2000 than in

other years.

Land use change was considered as main factor for spatial N budget change. However, changes occurred in the N budget in the centre of the urban land use (although land use did not change) during the study period. This is because this study only considered land use change and excluded other factors that have an impact on the N cycle, e.g. climate change and soil management. The magnitude of total source N budget of urban centre decrease may be associated with hydroclimatic characteristics since, as for example, Smith et al. (2007) point out that increases in temperature have been linked to increased loss of soil organic C which may cause increased loss of soil organic N (increased fluvial N loss). The increased fluvial N loss may lead decrease in the magnitude of source N budget decreased. Moreover, although the 1990 data is not compatible with the later data, according to CEH, the trend of different land use was proper during the study period (1990-2015). Therefore, the land use data from 1990 to 2015 was still can be used to forecast the trend of N budget in the future.

N gas emission was the greatest of all N outputs between 1990 and 2015 (Table 4.1). Part of this N gas emission was assumed to be deposit to the land and water surfaces, but the remainder was transported outside of the Trent catchment. The amount of N gas emission predicted to be transported outside the Trent catchment decreased from 108 $\times 10^3$ tonnes N in 1990 to 31 $\times 10^3$ tonnes N in 2015, accounting for 53% to 20% total anthropogenic Nr for those years, respectively. Total N fluvial loss was another way of transporting N out of the Trent catchment, and the N gas emission was nearly 1.5 or 3 times the total N fluvial flux. These two N component

fluxes account for more than 50% of the total N output. To understand N export outside of the Trent catchment, we should propose the greatest effort be placed into understanding factors impacting N gas emission and N fluvial loss rather than other N pathways. The N fluvial loss and N gas emission not only the major N export outside but also major N output pathway inland areas. Therefore, understanding the sources of N fluvial loss and N gas emission can mitigate N pollution problems in the coastal and inland areas of the Trent catchment.

## 4.4 Conclusions

The N budgets for the Trent catchment were negative (source area), with total N outputs exceeding total N inputs by about -43±7 $\times 10^3$ tonnes N in 1990. Over for the period 2000 – 2015, the total N budget for the Trent catchment was positive (sink area), with N inputs exceeding outputs by about 22±3 $\times 10^3$ tonnes N in 2000 and by 35±5 $\times 10^3$ tonnes N in 2015. Based on simple linear extrapolation, the magnitude of the total N budget increased at a growth rate of 3% per year from 2000 to 2015 and it is likely to continue in the future. The total excess N (total N input- total N output) increased by 13±7 $\times 10^3$ tonnes N between 2000 to 2015. Fertiliser was found to be the greatest contributor overall of all N input pathways, but fertiliser inputs decreased from 105 $\times 10^3$ tonnes N in 1990 to 76 $\times 10^3$ tonnes N in 2015. The total N atmospheric emission was the biggest contributor of all output pathways. This decreased from 125 $\times 10^3$ tonnes N to 47 $\times 10^3$ tonnes N over the period from 1990 to 2015. Spatially across the Trent catchment, source areas decreased from 77% of the total Trent catchment in 1990 to 31% of the total Trent

catchment in 2015. Sink areas increased from 23% of the total Trent catchment in 1990 to 69% of the total Trent catchment in 2015. Changes from sink areas to source areas were mainly caused by the conversion of grass land use to urban land use (urbanisation) and from grass land use to arable land use. Conversely, change from source areas to sink areas was caused by conversion from arable land use to grass land use. The Trent catchment has seen an increase in population and hence the magnitude of source N budget ($5 \times 10^{-3}$ tonnes N/yr per person). Moreover, when expanding urban land use is considered alone, then the total N budget of Trent catchment will transfer from sink to source in the future.

# Chapter 5

# The flux of nitrate and controls on total N budget

## 5.1 Introduction

It is widely accepted that intensification of agriculture makes a considerable contribution to water pollution (deterioration of drinking water and eutrophication), mainly by leaching and contaminant transport in surface runoff (Turner and Rabalais 1994; Vitousek et al. 1997; Burt et al. 2011). There are two common reasons for increasing N in rivers. First, intensification of agriculture deforestation has increased total N fluvial flux by increasing the rates of N mineralization and mobilization in soils (Williams and Melack 1997). Second, enhanced transfer of N from land to water is a consequence of increased N inputs to land, especially anthropogenic N inputs (Boyer et al. 2002). Anthropogenic N inputs have directly caused environmental problems (including the atmosphere and river systems). Howarth et al. (2012) estimated that approximately 25% of net anthropogenic N inputs were exported to

the river system. The export ratio was influenced by hydroclimate, land use type and human activities. To date, numerous studies have examined the relationship between N cycling and various human activities (Howarth et al. 1996; Filoso et al. 2006). In many countries, N inputs were controlled mainly by anthropogenic activities (i.e. fertilizer application, N deposition and BNF in agriculture) rather than being controlled by natural processes (i.e. natural BNF and lightning) (Galloway et al. 2004). Seitzinger et al. (2005) used an empirical approach to predict how natural and anthropogenic activities impact on N fluvial flux loss from land. This result demonstrated that anthropogenic N sources dominated the export of dissolved inorganic N at global scale and natural N source account for over 80% of DON export globally. In addition, as Worrall et al. (2016a) noted, previous studies (e.g. Whitmore et al. (1992b)) have demonstrated that the timescale for adjustments in net soil mineralization or immobilization caused by land use change, needs to be considered over a span of decades. It is reasonable to assume that the change of N fluxes could be decades. Therefore, the N fluvial flux should be considered across multiple years rather than limited to considering the N fluxes in only one year. Long term records of nitrate flux and all significant controls which may impact on nitrate flux are available for constructing models to enhance understanding how the controls impact on nitrate flux.

Worrall et al. (2009) showed that the UK was a hotspot for total N fluvial flux, with a higher export of dissolved N than any other region of comparable size in the world. To reduce the high potential dissolved N fluvial flux from the UK, We need to understand the key controls in order to target effective management intervention.

Numerous studies have explored the relationship between anthropogenic N inputs and total N fluvial flux (Boyer et al. 2002; David and Gentry 2000; Swaney et al. 2012). Anthropogenic N inputs are influenced by different catchment characteristics, e.g. land use, soil types, and hydroclimatic characteristics. It is useful to explore which catchment characteristics impact on N fluvial fluxes. Worrall et al. (2012a) estimated the empirical relationship between nitrate flux and catchment characteristics, but did not include hydrological characteristics. Moreover, atmospheric deposition and atmospheric emission of N species were not considered. In Chapter 2, the components of the total N budget were estimated across GB. Therefore, in this chapter the flux records reported by Worrall et al. (2012a) are updated and get an equation is presented for nitrate flux that includes the missing components of the N budget.

In previous chapters the N fluvial flux as a component of N budget, was estimated by use of the model of Worrall et al. (2012a). Due to the restricted data and time, it is impossible to improve the estimation of all N components; however, it is possible to improve the fluvial nitrate flux. Worrall et al. (2009) showed that total fluvial N flux comprised 69% nitrate. Thus, improving the estimation of nitrate flux can improve the total N budget. Worrall et al. (2012a) calculated the nitrate flux based on 122 catchments and did not use any components of the N budget. The aim of this chapter, therefore, was to improve the estimation of the nitrate flux by increasing number of catchments included in the analysis; upgrade the nitrate flux estimation to a low bias alternative; and by including independent N budget component (N deposition, N atmospheric emission). Specifically, this chapter aimed to: (1) improve

the nitrate flux from soils to the river network based on large sample sites and to establish a relationship between nitrate flux and catchment characteristics (including land use, soil types, N component and hydrologic characteristics), and (2) Identify end-members and compositional trends using principal component analysis (PCA) to identify controls on the processing of that nitrate fluvial flux.

## 5.2 Methods

The total N budget of each river catchment can be calculated by aggregating each 1km$^2$ N budget (Chapter 2) within catchment boundaries, which provided the flux of N component for every catchment. For this N budget, most of N pathways were directly linked to physical characteristics (land use, soil types, rainfall, base flow index and mean river flow) and others (e.g. gaseous emissions N and total atmospheric deposition of N) were independently derived. The nitrate fluvial flux was calculated for catchments, where the physical characteristics of the catchment and total N budget components were known. Where the average catchment nitrate flux could be calculated, for the period from 2005-2016, it was compared to a range of physical catchment characteristics and independently measured total N budget components and an empirical model was constructed. It is an attempt to assess controls on the nitrate flux. The 414 gauging stations were found to coincide with nitrate concentration monitoring locations in England. The chapter only considers data for England as a result the gauging station and nitrate concentration monitoring locations were only distributed across England.

### 5.2.1 Nitrate flux calculation

This study used datasets on nitrate concentration obtained from the Environment Agency. There are 8419 sites in GB from which it is possible to get an expected value of concentration. These sites were checked to see if they coincide with gauging stations, i.e. for where nitrate monitoring in rivers coincides with locations where river flows were being monitored. The majority of the 8419 sites did not coincide with a river flow gauging station and so it is not possible to calculate a nitrate flux for these. However, 414 gauging stations were found to be coincident with nitrate concentration monitoring locations for which an expected value could be calculated, and therefore, for which a nitrate flux could be calculated. The length of records available for the study was from 2005 to 2016. The average nitrate flux from 2005 to 2016 was considered here. Based on the nature of the sources of variation within the flow and solute datasets, flux calculations were carried out using the method of Worrall et al. (2013). This method preserved all the available flow information and had a low bias. The fluvial flux of nitrate was estimated by the equation:

$$F = \mathrm{K}\ \mathrm{E}(C_i)Q_{total} \tag{5.1}$$

where: $F$ = the N fluvial flux in tonnes N/yr; $Q_{total}$ = the total flow in a year ($m^3$/yr); $E(C_i)$ = the expected value of the sampled concentration (mg/l); and $K$ = constant for unit conversion (0.000001 for flux in tonnes N/yr). For the best results, the expected value of the sampled concentration was based upon the expected value of a gamma distribution.

### 5.2.2 N budget component and catchment characteristics

ArcGIS was used to extract catchment boundary and extract every component of the total N budget component aggregating for every 1 $km^2$ within catchment boundaries for the 414 catchments where it was possible to calculate a nitrate flux. The total N budget was defined as previously in Chapter 3, i.e. the inputs were: BNF, atmospheric N deposition, food and feed transfer, and inorganic N fertilizer. The outputs of N considered were: atmospheric N emission, terrestrial denitrification, N fluvial flux loss from the soil, N gas emissions from sewage treatment plants, direct sewage N flux loss, groundwater N loss, and industrial N loss. It was possible to give a value to each of these N budget components for each catchment. Most N pathways were assumed to be dependent on land use and soil type. Only two N pathways were considered independent (N deposition and atmospheric N emission).

In this chapter, the catchment properties considered were: land use, soil types and hydrological characteristics (rainfall, base flow index and mean river flow). The temperature is collinear with rainfall and river flow, therefore this chapter did not include temperature as an individual factor. Due to the availability of nitrate measurement points across England but limited availability in Scotland and Wales, this chapter considered England only. The land use for each 1 $km^2$ of England was classified into arable, grassland and urban (Defra, 2005). The soil types of England were classified into mineral, organo-mineral (OrgMin) and organic (Hodgson 1997). Land use and soil type data for 1 $km^2$ grid squares were as described in Chapter 2. For each of the catchments, for which a nitrate flux could be calculated, the following hydrological characteristics were used: rainfall, base flow index and river flow. The

mean annual rainfall was computed from the daily mean rainfalls using data only for years where the monthly rainfall record is complete. Base flow index is a measure of the proportion of the river runoff that derives from groundwater stored sources. It is computed by using the archived record of gauged daily mean flows. Mean gauged river flows at gauging stations were calculated by the average, weighted to account for the different number of days per month, of the mean monthly flows for the period of record ($m^3/s$). The hydrological characteristics for each catchment were available from the National River Flow Archive (`www.ceh.ac.uk/data/nrfa/`). This chapter estimated model of nitrate flux including catchment characteristics, N component and hydrological characteristics.

### 5.2.3 Statistical modelling and PCA

Multiple linear regression was used to predict the average annual nitrate flux and export for the period 2005 – 2016 from catchment characteristics ( 3 soil types; 3 land uses; and 3 hydrological characteristics). Modelling was performed with both explanatory variables and the response variable in both untransformed and log-transformed forms. Normality of transformed or untransformed variables was tested using the Anderson-Darling test (Anderson et al. 1952) and variables were only included in the model if they were statistically significantly different from zero at the 95% probability level. Stepwise regression was used for variable selection with both forward and backward selection and the probability for inclusion set at 95% chance of not being zero. Models were chosen both on the basis of model fit, as assessed by the coefficient of determination ($r^2$), and the physical-interpretability of the model.

The variance inflation factor (VIF) quantifies the severity of multicollinearity in the multiple linear regression analysis. The VIF can range from 1 upwards, and can be interpreted based on a rule of thumb (VIF value 1= not correlated; VIF value between 1 and 5 = moderately correlated; VIF value greater than 5 = highly correlated). A VIF of 10 is commonly set as the maximum level with a value greater than 10 is not acceptable (Hair et al. 2013). This chapter used VIF as a guide to select a variable in multiple regression.

The land use, soil type, hydrological data and N flux for the 414 sub-catchments were summarised into a multivariate data set. To further test the appropriateness of using multiple linear models to describe nitrate flux data from 414 catchments, principal component analysis (PCA) was used. PCA was used to assess which characteristics were most likely correlated with nitrate fluvial flux and whether the dataset was controlled by multiple relationships or that subsets existed in the data. The PCA used the mean annual rainfall, mean annual flow, base flow index, catchment area, arable, grassland, urban, mineral, organic, OrgMin, predicted gas emission, deposition and nitrate flux. In total, there were 13 variables and 5382 observations. The data included in the PCA were not normalised, standardised or transformed priority to analysis. A correlation matrix was used with only principal components with an eigenvalue larger than 1 included, and the first with an eigenvalue of less than 1, were considered for future examination. Principal components with eigenvalues $> 1$ represent more of the data set variance than any of the original variables (Chatfield and Collins 1980).

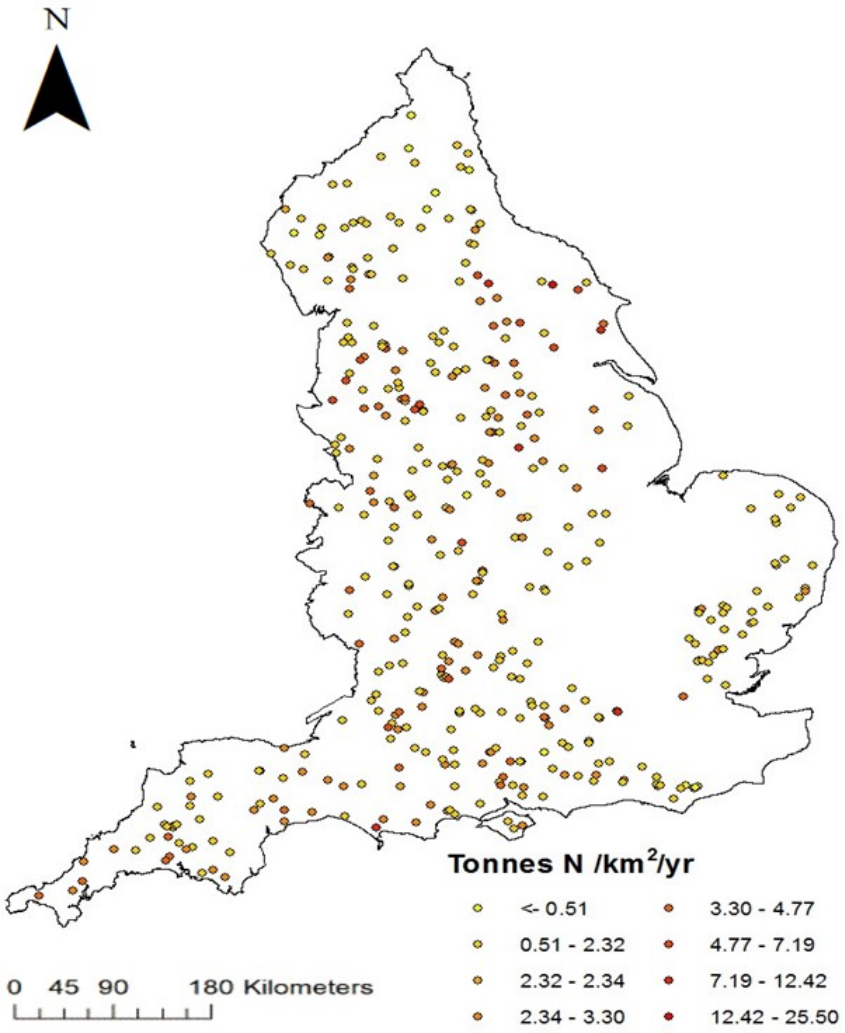


**Figure 5.1:** The locations of sites for which nitrate flux could be calculated and measured N export for each catchment.

## 5.3 Results

### 5.3.1 Nitrate–N ($NO_3$-N)

A total of 414 catchments were considered in the analysis of nitrate (Figure 5.1). Figure 5.1 shows the nitrate export ranged from 0.2 to 25.5 tonnes N $km^2$/yr.

The average annual nitrate flux from each catchment was compared to the avail-

able catchment characteristic (land use, soil type, hydroclimatic data and N budget component). The best-fit regression equation ($R^2$=89.14%, n=414) for nitrate was:

$$\begin{aligned} Nitrate_{flux} = & \underset{(15.9)}{32.2}\, Mean\ Flow + \underset{(0.2)}{1.7}\, Area \\ & + \underset{(0.8)}{8.1}\, Urban + \underset{(0.5)}{2.5}\, Organic \end{aligned} \tag{5.2}$$

where : $Nitrate_{flux}$ is the average annual nitrate flux (tonnes N/yr); *Mean Flow* is mean yearly flow ($m^3/s$) for the catchment; *Area* is the area of total catchment ($km^2$); *Organic* is the area of organic soils in the catchment ($km^2$). Only variables that were found to be significant at least at the 95% probability level were included in Eq. (5.2) and the numbers in the brackets are the standard errors of each coefficient. Eq. (5.2) could be interpreted as an export coefficient type of model. Eq. (5.2) suggests that the flux of nitrate was correlated with urban land use, catchment area and the organic soil. In other words, nitrate flux appears to with urban land use areas; with increasing catchment size and increasing areas of organic soils. Nitrate flux also has a negative relationship with mean flow (this strange situation will discuss in the discussion part).

Eq. (5.2) could not be directly extrapolated or mapped across England (since the parameter mean flow is not known across GB at a reasonable scale). Therefore, an alternative approach was proposed with only the land use variables (arable, grassland and urban) included. This can be mapped using only land use data, the best-fit equation ($R^2$=88.06%, n=414) was:

$$Nitrate_{flux} = \underset{(0.3)}{0.9}\, Arable + \underset{(0.2)}{2.4}\, Grassland + \underset{(0.7)}{9.9}\, Urban \tag{5.3}$$

where: *Arable* is the area of arable land in the catchment ($km^2$); *Grassland* is the area of grassland in the catchment ($km^2$); All other terms have the same meaning

as for Eq. (5.2). Although this equation has a marginally worse fit than Eq. (5.2) in term of $R^2$, the variables included are all significant at the 95% probability, and these are significant variables that are physically interpretable and can be mapped because the parameter each land use is known across GB at 1 $km^2$ scale and the positive coefficient of each land use is physically meaningful as land act as a source of nitrate. Interpreting Eq. (5.3) as an export coefficient model suggests that the urban land use was the dominant source of nitrate which would amount to an equivalent export of 9.9 tonnes N/$km^2$/yr. The model also suggests that grassland was a larger source of nitrate than arable land use. Extrapolating Eq. (5.3) across England gives a projected export of nitrate at the 1 $km^2$ scale and shows that the highest exports are predicted in the London area and the west of England (Figure 5.2). If the model fitting well, the residual should be normal with a mean of 0. Unfortunately, in this model the N flux and residuals were not normally distributed. Normality of N flux and residual was tested and showed in Figure 5.3, the Anderson-Darling test suggested it was necessary to log-transform the response variable prior to construction of the linear model. After log-transform, it successfully normalised the variables.

For the log-transformed nitrate data, the best-fit regression equation ($R^2$=55.66%, n=414) for nitrate:

$$\begin{aligned}\log_{10} Nitrate_{flux} = & \underset{(0.09)}{2.05} - \underset{(0.0005)}{0.0036}\,Grassland + \underset{(0.0002)}{0.0006}\,OrgMin \\ & - \underset{(0.00005)}{0.00028}\,Rainfall + \underset{(0.1)}{0.6}\,Base\ flow\ index \\ & + \underset{(0.01)}{0.11}\,Mean\ flow + \underset{(0.00003)}{0.00013}\,Emission\end{aligned} \tag{5.4}$$

where: *OrgMin* is the area of organic mineral soils in the catchment ($km^2$); *Emis-*

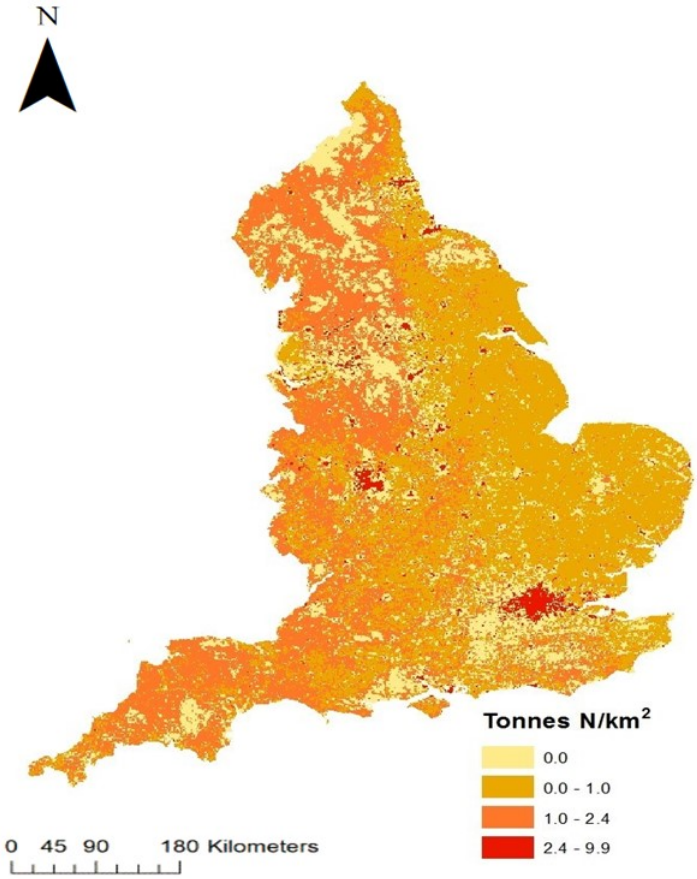


**Figure 5.2:** The map of nitrate export at the 1 km$^2$ scale assuming Eq. (5.3).

*sion* is the total N emission in the catchment (tonnes N/yr); *Rainfall* is total rainfall averaged over the catchment in millimetres (mm); *Base flow index* is a measure of the proportion of the river runoff that derives from stored sources. The variables included were still significant at the 95% probability. All other terms have the same meaning as for Eq. (5.2). However, in this equation, urban, grassland and catchment area descriptors were not significant variables. Because the VIF of grassland is very high (93), the grassland descriptor is collinear with other land uses and catchment area. The negative coefficient for the area of grassland may not reflect an absorption or sink of nitrate. The negative coefficient for grassland cannot be physically interpretable as grassland cannot act as a sink of nitrate (nitrate flux should be

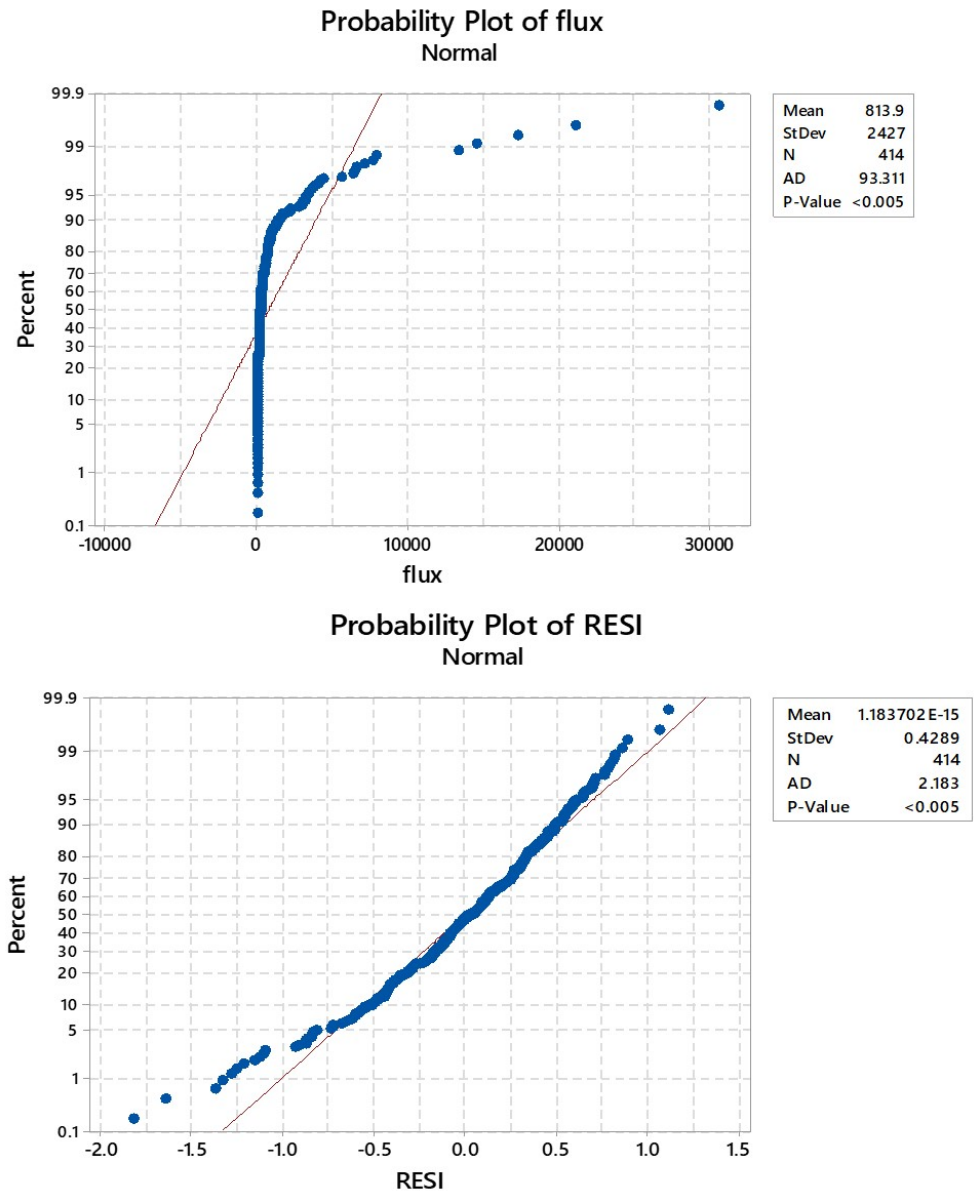


**Figure 5.3:** Normality test for nitrate flux and residual.

increasing with grassland area). This equation is not mappable because the base flow index and mean flow are not known across GB at a 1 km$^2$ scale.

Stepwise regression was performed with both untransformed nitrate export (defined as nitrate flux divided by area) and log-transformed nitrate export. In terms

of the annual average nitrate export, the best-fit equation: ($R^2$=6.85%, n=414) is:

$$Nitrate_{export} = \underset{(0.3)}{0.8} + \underset{(0.5)}{2.6}\, Base\ flow\ index \tag{5.5}$$

where all terms are as defined above.

The Anderson-Darling test suggested that it was necessary to log-transform the response variable prior to construction of the linear model (because the data of nitrate export was not normal). Log-transformation was able to improve the fit of the model. For the log-transformed nitrate export data, the best-fit equation ($R^2$=18.77%, n=414) is:

$$\begin{aligned} \log_{10} Nitrate_{export} = {} & \underset{(0.06)}{0.08} - \underset{(0.0003)}{0.0010}\, Grassland + \underset{(0.0003)}{0.0013}\, Urban \\ & - \underset{(0.00003)}{0.00009}\, Rainfall + \underset{(0.07)}{0.44}\, Base\ flow\ index \\ & + \underset{(0.007)}{0.039}\, Mean\ flow + \underset{(0.00002)}{0.00006}\, Emission \\ & - \underset{(0.00005)}{0.00024}\, Deposition \end{aligned} \tag{5.6}$$

where the *Deposition* is the N deposition in the catchment (tonnes N/yr) and a other terms are as defined above. Eq. (5.6) was not physically meaningful and mappable because the base flow index and mean flow are not known across GB at a 1 $km^2$ scale. Furthermore, a negative coefficient for grassland is not physically meaningful as land cannot act as a sink for nitrate. However, Eq. 5.6 can explain the relationship between nitrate flux and different catchment characteristics i.e. nitrate flux has a positive relationship with emission and negative relationship with deposition.

### 5.3.2 Principal component analysis

Principal component analysis was used to assess the multivariate structure of the data. In the PCA with all 13 variables, the first three principal components (two components with eigenvalues larger than 1, and the first with an eigenvalue less than 1) explained 90% of the original variance in the data (Table 5.1). From the loadings on the principal components, principal component 1 (PC1) is a general component with relatively high loading (loadings larger than 0.1) across all variables except for those associated with other components, i.e. mean rainfall and base flow index. The second component (PC2) has high positive loadings (loadings larger than 0.1) for base flow index, and high negative loadings (loadings less than -0.1) for mean rainfall, organic and mean flow. PC2 has a weak correlation (loadings less than magnitude 0.1) with Area, OrgMin, Gas emission, Deposition and Nitrate flux. The third component (PC3) has a higher magnitude loading for the Nitrate flux than PC2 (Table 5.1). The third principal component (PC3) has high positive loading (loadings larger than 0.1) for Base flow index, Mean flow, Organic, and OrgMin, and high negative loadings (loadings less than -0.1) for Urban and Mineral. PC3 has weak correlation (loadings less than magnitude 0.1) with mean rainfall, gas emission and deposition. Plotting the scores on PC1 and PC2 for all the catchments shows a clear pattern of differentiation (Figure 5.4). This helps confirm the interpretation of the components given above. Most data in Figure 5.4 only varies along PC2, which has a weak correlation with nitrate flux (loadings less than 0.1). Sub-catchments showed three trends. Firstly, the majority of catchment samples trend parallel to PC2 (line AB), which varies only in Mean rainfall, Base flow index, and Organic.

**Table 5.1:** The first three principal components for catchments across England (with nitrate flux).

| Variable | PC1 | PC2 | PC3 |
|---|---|---|---|
| mean rainfall (mm) | -0.016 | -0.599 | -0.074 |
| base flow index | 0.019 | 0.506 | 0.729 |
| mean flow ($m^3/s$) | 0.309 | -0.203 | 0.180 |
| area($km^2$) | 0.328 | 0.029 | -0.050 |
| arable($km^2$) | 0.306 | 0.172 | -0.192 |
| grassland($km^2$) | 0.321 | -0.080 | 0.071 |
| urban($km^2$) | 0.292 | 0.126 | -0.195 |
| mineral($km^2$) | 0.312 | 0.141 | -0.202 |
| organic($km^2$) | 0.149 | -0.518 | 0.536 |
| OrgMin($km^2$) | 0.295 | -0.026 | 0.136 |
| gas emission(tonnes) | 0.324 | 0.028 | -0.025 |
| Depositon(tonnes) | 0.328 | -0.022 | 0.012 |
| nitrate flux (tonnes) | 0.310 | 0.029 | -0.046 |

OrgMin and deposition of those catchments do not change considerably (loadings less than magnitude 0.01) in this trend (line AB). One end-member of trend 1 (point A) represents the high rainfall data and proportion of grassland in the whole data set with a rainfall of 3233 mm/yr and a percentage cover of grassland of 96% (Figure 5.4). The other end-member of Trend 1 (point B) has a rainfall of 740 mm/yr and a grassland percentage of 1% (Figure 5.4). Secondly, a trend (line AD)

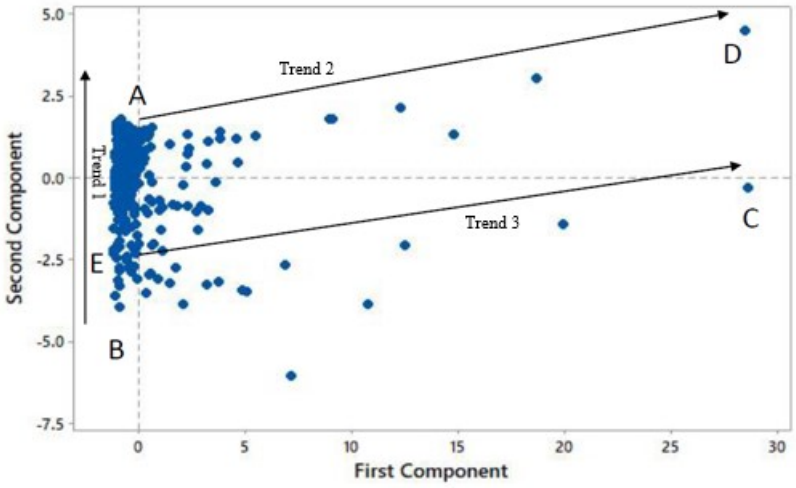


**Figure 5.4:** PC1 versus PC2 for the catchment data set.

was observed, which shares an end-member with Trend 1 (point A), but where PC 2 increasing was correlated with increasing PC1. Increasing PC1 was correlated with increasing total nitrate flux. This element (nitrate flux) that would appear in PC2 with increasing Arable land, Base flow index and decreasing with Rainfall, Grassland and Organic soil. Thirdly, Trend 3 (Line EC) followed Trend 2 outlined above, i.e. increasing positive score on PC1 were accompanied by an increasing score on PC2 (decreasing arable land and base flux index). All data on line EC plotted are lower at values of PC1 and PC2. Instead the Trend 1 represented variation in PC2, the Line AD and EC showed the relationship between PC1 and PC2. The deviation between Line AD and Line EC can be explained by differences in Grassland, Mean rainfall, Arable land, Organic soil and Base flow index. From Figure 5.4, it also implied that catchments plotted on Trend 2 and Trend 3 apart from the majority of catchments on Trent 1, implying these catchments areas are larger than others and deposition to these catchments is higher than to catchments located on line AB. The PCA did not

reveal details of nitrate flux, but it showed the contrast in catchment characteristics in terms of land use, soil type and hydrological characteristics. The PCA carried out in this chapter did not show any distinction between catchments and did not pick out any catchment clusters of catchment. This result is same as the equations (Eq. 5.2 to Eq. 5.6), these equations did not show any catchment clusters of catchments. The use of PCA illustrated that there are no clusters of catchments with respect to nitrate flux, and that the multivariate linear regression is appropriate. Furthermore, PCA was also performed with log-transformed nitrate flux. Specifically, the first three principal components (two components with eigenvalues larger than 1, and the first with an eigenvalue less than 1) explained 87% of the total original variance in the data (Table 5.2). Principal component 1 is a general component with relatively high loading (loadings larger than magnitude 0.1) across all variables except for mean rainfall and base flow index. The use of PCA also illustrated that there are no clusters of catchments with respect to log-transformed nitrate flux.

In Figure 5.4, most catchments plotted along Trend 1, with a few following Trend 2 and Trend 3. The PCA suggested there is a distortion caused by Trend 1 and Trend 2. Therefore, it is perhaps advisable to remove the data from Trend 2 and Trend 3 and reanalyse the data. The catchments on Trend 1 and Trend 2 have large areas and large nitrate fluxes which distorted the calculations. This study removed 10% of data without distorting overall data. After removal of the data on Trend 1 and Trend 2, the PCA did not found any further details (Table 5.3) and still show a similar result with before removal of data. Specifically, the first three principal components (two components with eigenvalues larger than 1, and the first with an

**Table 5.2:** The first three principal components for catchments across England (with log-transformed nitrate flux).

| Variable | PC1 | PC2 | PC3 |
|---|---|---|---|
| mean rainfall (mm) | -0.018 | -0.601 | -0.102 |
| base flow index | 0.025 | 0.516 | 0.549 |
| mean flow ($m^3/s$) | 0.320 | -0.199 | 0.130 |
| area($km^2$) | 0.335 | 0.027 | -0.101 |
| arable($km^2$) | 0.312 | 0.169 | -0.222 |
| grassland($km^2$) | 0.330 | -0.079 | 0.004 |
| urban($km^2$) | 0.296 | 0.122 | -0.204 |
| mineral($km^2$) | 0.317 | 0.136 | -0.247 |
| organic($km^2$) | 0.157 | -0.510 | 0.471 |
| OrgMin($km^2$) | 0.305 | -0.022 | 0.107 |
| gas emission(tonnes) | 0.332 | 0.027 | -0.079 |
| Depositon(tonnes) | 0.336 | -0.022 | -0.033 |
| $\log_{10}$nitrate flux (tonnes) | 0.222 | 0.046 | 0.518 |

eigenvalue less than 1) explained 80% of the total original variance in the data (Table 5.3). Principal component 1 was still a general component with relatively high loading (larger than magnitude 0.1) across all variables except for mean rainfall and base flow index. Figure 5.5 still showed some catchments that did not follow the main trend (Line FG). However, caution was taken when removing more data from a dataset in order to avoid distorting the dataset too much. Therefore, the

**Table 5.3:** The first three principal components for catchments across England (after removed outlier).

| Variable | PC1 | PC2 | PC3 |
|---|---|---|---|
| mean rainfall (mm) | -0.016 | -0.607 | -0.028 |
| base flow index | 0.021 | 0.515 | -0.768 |
| mean flow ($m^3/s$) | 0.312 | 0.199 | -0.148 |
| area($km^2$) | 0.327 | -0.024 | 0.050 |
| arable($km^2$) | 0.300 | -0.181 | 0.211 |
| grassland($km^2$) | 0.322 | 0.075 | -0.046 |
| urban($km^2$) | 0.290 | -0.094 | 0.111 |
| mineral($km^2$) | 0.309 | -0.137 | 0.203 |
| organic($km^2$) | 0.150 | 0.511 | -0.519 |
| OrgMin($km^2$) | 0.295 | 0.011 | -0.105 |
| gas emission(tonnes) | 0.324 | -0.039 | 0.063 |
| Depositon(tonnes) | 0.327 | 0.030 | -0.025 |
| Nitrate flux (tonnes) | 0.316 | -0.025 | -0.006 |

linear model of nitrate flux or export could not be improved after removal of the data on Trend 1 and Trend 2.

## 5.4 Discussion

Models designed (Eq. 5.4 and Eq. 5.6) in this chapter are an update of Worrall et al. (2012a), which included 414 sub-catchments more than the 115 used in Worrall et al.

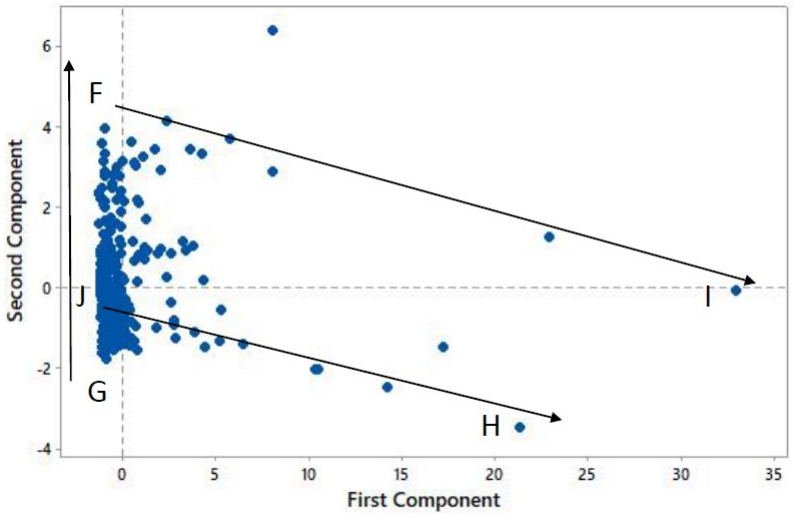


**Figure 5.5:** PC1 versus PC2 for the catchment data set after removed outlier.

(2012a). The updated model also includes N deposition, gas emission and rainfall, which can help us to understand controls on nitrate flux better. Many other studies have also constructed N export coefficient models, but these studies did not include N deposition and nitrate derived from different land uses caused by net mineralization of soil organic N (Johnes et al. 1996; Worrall and Burt 1999; Worrall and Burt 2001;Weber et al. 2006). Worrall et al. (2012b) constructed an N export coefficient model including N deposition and N derived from net mineralisation of soil organic N; therefore N export coefficient model of Worrall et al. (2012b) was more accurate than previous studies which did not include N deposition and nitrate derived from net mineralisation of soil organic N. During the process of calculating the export coefficient model, Worrall et al. (2012b) added average total atmospheric deposition of N to all land use. However, N deposition does not occur equally on all land uses. This study updated the N model of Worrall et al. (2012a) by including N deposition based on different land uses, N gas emission and hydroclimatic characteristics (rain-

fall, base flow data and mean river flow) and showed the relationship between nitrate flux and different controls. For hydroclimatic characteristics, summer drought and extreme precipitation events would affect the loading and processing of N within rivers and estuaries. Lower river flows may reduce the total N flux entering coastal regions, whereas higher flows will accelerate loading of N from terrestrial to aquatic systems. Eq. (5.3) suggests that the nitrate flux has a significant positive relationship with N deposition and significant a negative relationship with N gas emission. For N deposition, with an increase in the amount of applied N, net mineralization and N available for nitrate fluvial flux increase. The N deposition was negatively correlated with nitrate flux. This could be because that the N deposition may increase the root weight as well as an increase in the number of micro-organisms around rhizosphere (Tulloss and Cadenasso 2016). The increase in total root weigh and in number of micro-organisms around rhizosphere may decrease the decomposition of organic matter and then decrease the mineralization of N. Therefore, the N fluvial flux would decrease with increase in N deposition. In addition, the positive relationship between nitrate fluvial flux and gas emission could be explained by the soil C/N ratio. When the soil stores are disturbed by urbanisation or intensifying agricultural, there maybe loss C just a loss N (Bell et al. (2011)). The N gas emission may decrease the C/N ratio of organic matter in the soil, and, when the C/N ratio of below 20 usually leads to net mineralization (Stevenson and Cole (1999)). Thus, the N gas emission may increase the N available for nitrate fluvial flux. High nitrate flux was highly correlated with the extent of urban land, which is consistent with the result of Worrall et al. (2012a) and Davies and Neal (2004). Both Worrall

et al. (2012a) and Davies and Neal (2004) showed the urban land appears to have the highest export of nitrate of all land uses. However, Ferrier et al. (2001) found that nitrate flux was highly correlated with the extent of arable land. The result of Ferrier et al. (2001) was different with other studies can be explained by the inherent factors (soil drainage, soil texture and slope steepness) affecting availability to N loss as all nitrate fluvial flux studies did not consider the inhere factors. The inherent factors such as soil drainage, soil texture, and slope steepness impact N transformation processes that limit availability to N loss (N fluvial loss). These different inhere factors might impact which land use was the largest nitrate export.

## 5.5 Conclusions

In this chapter records of nitrate flux from 2005 to 2016 for 414 catchments in England were used to build regression models between N flux and catchment characteristics. The equations of nitrate flux explained up to 89% of the variation in nitrate flux across the 414 catchments, which provided significant export coefficients for urban, grass, arable as well as for organic soils. Nitrate export from any land use or soil type is also influenced by N deposition, N gas emission and rainfall. The nitrate export estimated in this chapter ranged from 0.2 tonnes N/km$^2$/yr to 25.5 tonnes N/km$^2$/yr. The N deposition and rainfall had a negative relationship with nitrate flux. In contrast, Area, Organic, land use areas and Gas emission had positive relationships with nitrate flux. Urban land use was the dominant control factor controlling nitrate flux.

# Chapter 6

# Conclusion and prospects

The research presented in this thesis consists of four topics with the aim of further understanding N cycles in our environment. Human activities have greatly altered the biogeochemical N cycle. Increased anthropogenically-sourced N is needed to meet global demands for food and energy but has resulted in an increase in the amount of Nr transfer to the atmosphere to freshwater and the marine environment. This has created a series of environmental problems (e.g. ozone layer destruction catalysed by $N_2O$, rising atmospheric greenhouse gas concentrations from $N_20$, acid rain, eutrophication of rivers, lakes, and sea, drinking water compliance and groundwater pollution). This thesis analysed the characteristics of N budgets at national and catchment scales considering all significant pathways of the N cycle. The findings of this study have led to an improved understanding of the anthropogenic N problem. This chapter summarises the main conclusions of this thesis, analyses the study's limitations, and proposes some potential future research.

## 6.1 Conclusions

This research was the first to construct a spatial total N budget at a 1 $km^2$ resolution for an entire country revealing the spatial pattern of N accumulation and loss. The total N budget at $1km^2$ ranged from -21 ± 3 tonnes N/$km^2$/yr to 34 ± 5 tonnes N/$km^2$/yr in GB. Sink areas (input >output), or N accumulation areas, were mainly located in western GB, accounting for 34% of total GB grid squares. Conversely, source areas (input <output), representing a net N loss to the surrounding atmosphere and marine environments, were predominantly located in eastern GB, accounting for 66% of total GB grid squares. 97% of urban areas were identified as source areas, 98.5% of arable land use areas were identified as source areas, and 34% of grassland areas were identified as sink areas. Therefore, the status of the N budget is likely to change with land use changes. The urban land use might increase in the future.

Overall, the total GB N budget represented a net source of -1045 ± 244 $\times 10^3$ tonnes N/yr in 2015. Fertilizer accounted for 60% of total N input and was the largest N input identified in the study. Fluvial N loss and atmospheric N emission were identified as the largest N outputs, accounting for 48% and 22% of total N export, respectively.

This thesis also determined the spatial N budget for the Trent catchment and provided primary data (local measurement data) on N fluvial loss and groundwater N loss in the catchment. The accumulation of total N in the Trent catchment was estimated to be 35 ± 5 $\times 10^3$ tonnes N in 2015. In the Trent catchment, 69% of

grid squares were identified as sink areas, and 31% were identified as source areas. With respect to N inputs, fertilizers contributed the largest N input both in the Trent catchment and for the whole of GB. With respect to N outputs, atmospheric N emission contributed 55% of total N output. It was the largest N output, higher than the contribution of atmospheric N emission from GB. The higher gas emission contribution was attributed to the higher proportion of arable areas in the Trent catchment relative to GB. Fluvial N loss from the Trent catchment accounted for 33% of the total N output, which is less than the proportion of fluvial N loss from GB.

Within the Trent catchment, the locations in which N accumulation occurred was investigated. On the basis of the constructed spatially differentiated total N budget, areas of accumulation and loss under different land uses were compared by analysis of the C/N ratio of their soil profiles. For the areas of net total N accumulation in the Trent catchment, it was hypothesised that subsoil C/N ratio would be significantly lower than the C/N ratio in the subsoil of areas identified as being of net total N loss. To test this hypothesis, a four-factor analysis of variance (ANOVA) was performed with C/N as the response variable. The expected result was that the two-way interaction term between N budget status (sink or source) and depth would be significant. In this case the C/N ratio should be lower at depth in the sink areas compared to source area. In reality, the depth profile only had a significant affect on the C/N ratio between sink areas and source areas under grassland. For arable land, no significant difference was observed between the subsoil C/N ratio of sink versus source areas.

Temporal variability in the Trent catchment N budget revealed the impact of land use change on the status of the N budget. Although the magnitude of both N input and N output decreased from 1990 to 2015, the N budget changed from -43 $\pm$ 7 $\times 10^3$ tonnes N to 35 $\pm$ 5 $\times 10^3$ tonnes N with the magnitude of total N output declining faster than total N input. For N input, fertilizer was the largest contributor to total N input, followed by human N consumption, BNF, atmospheric N deposition, and livestock N input. For N output, atmospheric N emission was the largest contributor to total N output, followed by crop N removed, total fluvial N loss, denitrification, and groundwater N loss. Over the study period, land use change impacted on the status of the N budget. Specifically, 65% of areas in the Trent catchment showed a decrease in the magnitude of net source N budget. These were dominantly in agricultural areas. In addition, 17% of the areas in the Trent catchment showed a decrease in the magnitude of sink N budget, these areas occurred near cities mainly caused by urbanization (grass change to urban and arable change to urban). While, 18% of areas in the Trent catchment showed a decrease in the magnitude of the source N budget, an increase in the magnitude of the sink N budget and a transferred status of the N budget (sink changed to source and source changed to sink). Overall, arable land use had the largest decrease in area over the study period (i.e. 1990 to 2015) with 1,300 $km^2$ areas changed from arable to other land uses (urban, grass and other). Arable land use change was ,therefore, the main reason for changing net source N flux from -43 $\pm$7 $\times 10^3$ tonnes N in 1990 to net sink in 2015 at 35 $\pm$ 5 $\times 10^3$ tonnes N.

To improve the accuracy of the N budget, all N fluxes need to be better esti-

mated. In this study, only the nitrate fluvial flux was updated. The nitrate flux for the country was recalculated using multiple regression analysis, and the nitrate export ranged from 0.2 tonnes N/km$^2$/yr to 25.5 tonnes N/km$^2$/yr. This study also constructed a regression model by comparing nitrate flux from 2005 to 2016 with catchment characteristics. This model provided significant export coefficients for urban areas, grassland, arable land as well as for organic soils. Rainfall and N deposition appeared to have a negative relationship with nitrate flux as inherent factor impact on nitrate loss from soil. Furthermore, the total catchment area, organic soil and gas emission has a positive relationship with nitrate flux. Urban land use was the dominant control factor for nitrate flux.

## 6.2 Limitations of the research

In the present study, biogeochemical N cycling was affected by land use, hydroclimate, and topography. Although this thesis used a large amount of data to estimate the N budget at a national and large catchment scales, there is a large variation in some of the estimated N fluxes (the uncertainty is huge for some N fluxes). To be more specific, denitrification to $N_2$ was estimated based on a review by Barton et al. (1999), but the uncertainty in denitrification was ±96% for each land use type. Unfortunately, because the study of Barton et al. (1999) has not been updated in recent studies and there is no other information about denitrification rate, the estimated annual $N_2$ denitrification rate is very imprecise represent N removed by denitrification. A thorough discussion on the process of denitrification is far beyond the scope of this thesis. This thesis assumed that the eventual product of denitrifica-

tion is $N_2$, even if the eventual emission was the less reduced form $N_2O$. Because this thesis was primarily concerned with the total N budget and not individual N species, the conversion of $N_2O$ to $N_2$ does not alter the mass of N loss by denitrification. $N_2O$ is an important greenhouse gas that catalyses stratospheric $O_3$ degradation, therefore, a more accurate estimation of it should be explored in future research in order to improve management of greenhouse gas emissions.

Some of N flux data used in this thesis were collected from government and research publications. However, there is considerable uncertainty in the data itself. In some cases, no error or uncertainty estimate was given by the data source, and a default uncertainty of ±80% that was assumed in this thesis is generous. As a result, this estimated N flux data with large uncertainty has an impact on the accuracy of the N budget calculated herein. Uncertainty in estimated N flux also has implications for future trends of the N budget in the Trent catchment. In addition, the catchment spatial N budget trend is forecast based on four years of data, 4-years N budget data is too small for forecasting the spatial N budget trend. In this study, due to the restricted data and time, this thesis has not updated all N components. The model of nitrate flux was updated for England in this thesis as sufficient local river flow, and concentration data were available.

The current policy of importing wood pellets from the U.S to burn instead of coal, also represent a new flux of N into GB from outside its boundary. There is no information on how to distribute the N flux from wood pellets to a 1 $km^2$ resolution, therefore, this study did not include the N flux from wood pellets. N input from rock weathering is also not included in this study. Houlton et al. (2018)

have calculated the N input from rock weathering for the Earth's surface and the N denudation flux was predicted as to be between 11 and 18 $\times 10^6$ tonnes N/yr. According to the total N denudation flux of the Earth's surface and total surface area of the Earth, the average export from rock weathering would be between 21 to 3.5 $\times 10^{-3}$ tonnes/km$^2$/yr. Therefore, the export of N input from rock weathering is relatively low when compared to other N pathways, and this N flux cannot be distributed to various land uses with a 1 km$^2$ spatial resolution.

## 6.3 Future work

This thesis has improved current estimates of nitrate fluxes for GB, England and the Trent catchment. To obtain a more precise N budget, currently available N flux data (e.g., from the literature and online databases) must be augmented through future catchment-scale field studies. The denitrification error estimate was the largest uncertainty found for any N input and output. Although 95% confidence interval was constructed for total N budget in this study, decreasing the uncertainty for every significant N pathway is recommended in a future study. The largest uncertainty should be a priority to settle out. Therefore, it is strongly recommended that the acetylene inhibition technique be used to measure the denitrification based on different land uses in GB to more accurately estimate $N_2$ flux removed by denitrification.

The N biogeochemical cycle has been transformed by human use of Nr. To improve quantitative estimates of the impact of human activities on the export of Nr, future studies should focus on calculating an N footprint at the personal, regional and country scale. An N footprint is the total amount of Nr released to

the environment as a result of an entity's consumption patterns. The N footprint can be comprehensively quantified in GB with an N mass balance approach. The N Calculation of an N footprint would improve understanding of an individual's impact on the N cycle and enable individuals to reduce their N-footprint (e.g. by lifestyle choices such as reducing food waste). Improving awareness of the role that humans play in the N biogeochemical cycle and the environmental and health consequences of N pollution could reduce current levels considerably.

This thesis has identified N accumulation areas across GB. However, this thesis was primarily concerned with the total budget and has not identified the source of N accumulation in the soil or groundwater. Stable isotope abundances of $^{15}N$ used to provide information on the origins and transformations of N in soil and groundwater. The fractionation of $^{15}N$ through biotic and abiotic processes contributes to different range of $^{15}N/^{14}N$ ratios for different N source. By analysing the range of $^{15}N$ of different N source (e.g. fertiliser, animal waste, soil N), it is easy to identify the source of N accumulation. Therefore, the use of the N isotope method (stable isotope $^{15}N$) to identify the source of accumulation N is recommended for future work. In the present study, fluvial N loss was found to be the largest N export in GB. To control N pollution of surface water, future studies should use the N isotope technique to identify the source and fate of N pollution in surface water.

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# Appendix A

# Permission letter

Dear Sir or Madam:

First of all, I would like to take this chance to thank you for taking the time to read my letter. I am a PhD student in the Department of Geography, University of Durham under the supervision of Prof. Fred Worrall from the Department of Earth Sciences also at Durham University(`https://www.dur.ac.uk/earth.sciences/staff/?id=386`). My research is in to how nitrogen cycles through our natural environment and I am writing to enquire whether I could have your permission to take soil samples from your land? Sampling will consist of the collection of 2 soil cores. These cores will be 3-inches wide and approximately 40-inches deep and will be collected using hand held equipment. The soil will be submitted for laboratory analysis of its organic matter content: I will be happy to supply you with any results after analysis. In taking the soil cores we will endeavour to minimise disturbance and would be happy to discuss any particular access restrictions you would require. I would hope to access your land for sampling either at the end of January or in early February 2018. If you are happy for me to have access to your land for this soil

sampling please could you email me at xiangwen.fan@durham.ac.uk, or my supervisor at Fred.Worrall@durham.ac.uk, or telephone us on 0191 334 2295, and then we can arrange a mutually agreeable time for access. Thank you for your attention and I hope for hearing from you soon.

Yours faithfully,

Xiangwen Fan

Fred Worrall

# Appendix B

# Location of farmland for sampling

| Name of farmland: | Postcode |
|---|---|
| Brecks Farm | NG22 0BP |
| Inkersall Farm | NG22 8TL |
| Villa Real Farm | NG21 9HE |
| Thoresby Park | NG22 9EW |
| Haywood Oaks Farm | NG21 0PE |
| Whitehouse Farm | NG22 9QJ |
| Beck Farm | DN17 2FN |
| Low Farm | DN22 8SB |
| Limpool Farm | DN11 9HQ |
| Spittalmoor Forest Farm | DN22 8DP |
| Crook Ford Farm | DN22 8BT |

| Name of farmland | Postcode: |
|---|---|
| Hexthorpe Park | DN4 0HY |
| Foremark Park Farm | DE73 7JP |
| Newclose Farm | DE4 3QY |
| Overfields Farm | DE12 8HB |
| Malt House Farm | DE12 8HN |
| West View Farm | LN1 2AN |
| None | S80 3PE |
| Green Farm | ST14 8DP |
| Kerfinch Farm | ST14 8QF |
| Woodland Hall Farm | ST14 8JX |
| Start Farm | LE10 3JA |
| Rectory Farm | WS15 3NW |
| Bromley Wood Farm | WS15 3AG |

# Appendix C

# Elemental Analyser

Thermo Scientific Flash 2000 Organic Elemental Analyser and NC (Nitrogen Carbon) Soil Analyser. This instrument is based on the process of dynamic flash combustion for the determination of carbon, hydrogen, nitrogen, sulphur and oxygen in solid samples. Samples are freeze-dried, ball-milled and are weighted(1-50mg) into tin capsules. arbon, hydrogen, nitrogen and sulphur analysis can be carried out simultaneously using the same combustion reactor. The samples are dropped one by one into the instrument's combustion reactor by an autosampler. The samples combust at temperatures of approximately 950°C in the presence of a small volume of oxygen in order to convert the sample into elemental gases. The gases then flow through a gas chromatographic separation column, where they are separated and are detected sequentially by a thermal conductivity detector.In order to increase the sensitivity of sulphur determinations a Flame Photometric Detector (FPD 112) is used in conjunction with the Flash 2000. This instrument has a detection limit of 0.5% .

# Appendix D

# Publication

Fan, Xiangwen, Fred Worrall, Lisa M. Baldini, and Tim P. Burt. "A spatial total nitrogen budget for Great Britain." Science of The Total Environment (2020): 138864.

Fan, Xiangwen, Fred Worrall, Lisa M. Baldini, and Tim P. Burt. (submitted) Spatial variability in the Trent catchment nitrogen budget: Identify areas of nitrogen accumulation and loss. Geoderma.